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Cleavage of Cyclodimethylsiloxanes by Dialkylaluminum Hydrides and the Nature of the Siloxyaluminum Products

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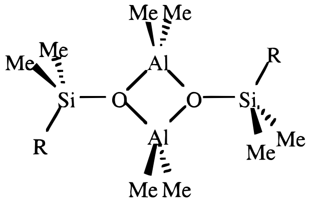
The interaction of R_2AlH with cyclic siloxanes leads to rupture of the silicon−oxygen framework and yields aluminum polysiloxides. The room-temperature reaction of R_2AlH with $(Me_2SiO)_3$ yields the asymmetrical siloxide compounds $R_2Al(\mu\text{-}OSiMe_2H)(\mu\text{-}OSiMe_2OSiMe_2H)AlR_2$, R = ^tBu (**1**), ^iBu (**2**). In contrast, the reaction of $(^tBu)_2AlH$ with $(Me_2SiO)_3$ or $(Me_2SiO)_5$ in refluxing toluene yields $[(^tBu)_2Al(\mu\text{-}OSiMe_2H)]_2$ (**4**), as does the reaction of $Al(^tBu)_3$ with $(Me_2SiO)_3$. $Me_2Al(\mu\text{-}OSiMe_2H)(\mu\text{-}OSiMe_2OSiMe_2H)AlMe_2$ (**3**) is formed from the reaction of Me_2AlH with $(Me_2SiO)_3$ in hexane when using a reagent Si:Al ratio of 0.5; higher Si:Al ratios result in the formation of the siloxide-bridged compound $Me_2Al(\mu\text{-}OSiMe_2H)AlMe_2(\mu\text{-}OSiMe_2O)Me_2Al(\mu\text{-}OSiMe_2H)AlMe_2$ (**5**). The asymmetrical polysiloxide compound $(^tBu)_2Al(\mu\text{-}OSiMe_2H)(\mu\text{-}OSiMe_2OSiMe_2OSiMe_2H)Al(^tBu)_2$ (**6**) is formed from the reaction of $(^tBu)_2AlH$ with $(Me_2SiO)_4$, while compound **5** and its isobutyl analogue (**7**) are formed with Me_2AlH and $(^iBu)_2AlH$, respectively. Reaction of R_2AlH with $(Me_2SiO)_5$ yields the siloxide-bridged compounds $R_2Al(\mu\text{-}OSiMe_2H)AlR_2(\mu\text{-}OSiMe_2OSiMe_2O)R_2Al(\mu\text{-}OSiMe_2H)AlR_2$, R = ^tBu (**8**) and ^iBu (**9**). If the reaction of $(^tBu)_2AlH$ with $(Me_2SiO)_5$ is carried out in the presence of THF, then $(^tBu)_2Al(\mu\text{-}OSiMe_2H)Al(^tBu)_2(\mu\text{-}OSiMe_2OSiMe_2O)Al(^tBu)_2(THF)$ (**10**) may be isolated. The reaction of Me_2AlH with $(Me_2SiO)_5$ yields compound **5**. The symmetric siloxide $[(^tBu)_2Al(\mu\text{-}OSiMe_3)]_2$ (**11**) is formed from the reaction of $(^tBu)_2AlH$ with $(Me_3Si)_2O$. The reaction of the noncyclic siloxane $Me_3Si(OSiMe_2)_2OSiMe_3$ yields a mixture of $(^tBu)_2Al(\mu\text{-}OSiMe_2H)(\mu\text{-}OSiMe_3)Al(^tBu)_2$ (**12**) and $(^tBu)_2Al(\mu\text{-}OSiMe_2H)(\mu\text{-}OSiMe_2OSiMe_3)Al(^tBu)_2$ (**13**). A combination of ^1H, ^{13}C, ^{27}Al, and ^{29}Si NMR allow for characterization of all compounds. In addition, the ^{29}Si NMR spectra of compounds **1**−**3** and **6** exhibit unusual $^3J(Si-H)$ coupling (1.0 Hz), and the Al_2O_2 core is found to exhibit a large deshielding effect on adjacent silicon. The molecular structures of compounds **1**, **4**, **8**, **10**, **11**, and **12** have been determined by X-ray crystallography. The reaction pathway for the cleavage of polysiloxanes is discussed.

Introduction

In 1959 Jenkner reported[2] that the reaction between $AlEt_3$ and $(Me_2SiO)_n$ yielded, upon hydrolysis, ethyl-substituted polysiloxanes, presumably via alkylation of the Si−O−Si linkage. It was subsequently shown that a similar reaction occurred via the formation of aluminum-containing species, eq 1.[3]

$$AlEt_3 + (MeHSiO)_n \rightarrow Et_2Al(OSiHMeEt) \qquad (1)$$

We have shown that the products from the cleavage of poly(diorganosiloxanes) with $AlMe_3$ are dimeric aluminum siloxides (**I**) resulting from methyl transfer from aluminum to silicon.[4] Similar results were subsequently reported by Mulhaupt et al.[5] In both cases no silicon-containing side products were isolated, all the siloxane being consumed in the reaction. This is in contrast to the results reported by Bissinger et al.[6] for the asymmetric cleavage of $(RH_2Si)_2O$ by Me_2AlCl, in which chlorosilanes are formed as side products (eq 2). Similar results were observed for the cleavage of $(RH_2Si)_2O$ and $(R_2HSi)_2O$ with AlX_3 (X = Cl, Br, I).[7]



(**I**)

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[1] (a) Rice University. (b) University of Houston. (c) Universität Göttingen.

[2] Jenkner, H. *Z. Naturforsch.* **1959**, *14*, 133.

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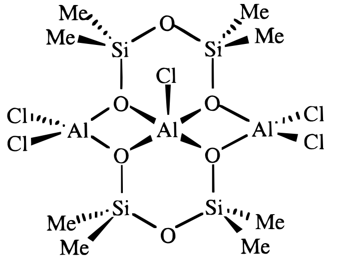
$$2(RH_2Si)_2O + 2Me_2AlCl \rightarrow [Me_2Al(\mu\text{-}OSiH_2R)]_2 + 2RH_2SiCl \quad (2)$$

The elimination of Me_2SiCl_2 and the dichlorosiloxane, $(Me_2ClSi)_2O$, from the reaction of $AlCl_3$ with $(Me_2SiO)_3$ and $(Me_2SiO)_4$, respectively,[8] resulted in the formation of a trialuminum siloxide compound (**II**) in which the Si:O ratio is less than unity.[9,10] An extension of this concept was recently reported by Wehmschulte and Power,[11] in which the reaction of the sterically demanding alkylaluminum dihydride $[(Mes^*)Al(H)(\mu\text{-}H)]_2$ with $(Me_2SiO)_3$ yields the alumoxane $[(Mes^*)Al(\mu\text{-}O)]_4$.[12] Although this alumoxane shows no activity in Kaminsky-type[13] metallocene polymerization catalysis, there have been several reports of the synthesis of catalytically active siloxy-substituted methylalumoxanes via the cleavage of poly(organosiloxanes): two methods have been employed to this end. First, the reaction of methylalumoxane (MAO) with poly(organosiloxanes) results in increased solubility of the MAO.[14] Second, hydrolysis of $[Me_2Al(\mu\text{-}OSiR_2Me)]_2$ yields stable, soluble, siloxy-substituted methylalumoxanes.[15] This latter method was previously published as part of a study in the preparation of siloxy-substituted alumoxanes.[16,17]



(**II**)

Despite the beneficial (and detrimental[18]) potential application of the cleavage of poly(diorganosiloxanes) with aluminum alkyls and hydrides and the structural characterization of the final products,[4−7] there is little understanding of the pathway involved in this conceptually simple reaction. To gain a better understanding of the reaction steps and attempt to isolate intermediates on going from the poly(diorganosiloxane) and the aluminum siloxide (**I**), we have investigated the reactivity of dialkylaluminum hydrides R_2AlH ($R = {}^tBu$, ${}^iBu$, Me) with cyclic siloxanes $(Me_2SiO)_n$ ($n = 3, 4, 5$).

Results and Discussion

Reaction of R_2AlH with $(Me_2SiO)_3$. Reaction of R_2AlH ($R = {}^tBu$, ${}^iBu$, Me) with $(Me_2SiO)_3$ in hexane yields after 3 days at room temperature the asymmetrical siloxide compounds $R_2Al(\mu\text{-}OSiMe_2H)(\mu\text{-}OSiMe_2OSiMe_2H)AlR_2$, $R = {}^tBu$ (**1**), ${}^iBu$ (**2**), Me (**3**); see Scheme 1. It should be noted that compound **3** is formed only if the Si:Al ratio is 0.5 (see below). Compounds **1**−**3** have been characterized by mass spectrometry and IR and NMR spectroscopy (Tables 1 and 2); see Scheme 1 for assignments. The mass spectrometries of compounds **1**−**3** are all consistent with the formulated structures, while the molecular structure of compound **1** in the solid state has been confirmed by X-ray crystallography (see below).

The IR spectra of compounds **1**−**3** each show a band consistent with a ν_{Si-H} stretch [2149 cm^{-1} (**1**), 2150 cm^{-1} (**2**), 2145 cm^{-1} (**3**)]. Unfortunately the resolution is insufficient to resolve the two chemically distinct Si−H groups present in each compound. However, the ^1H NMR spectra of **1** and **2** (Table 1) each show two distinct septets, in the range 4.9−4.7 ppm, due to silicon hydrides, confirming the presence of two magnetically inequivalent $OSiMe_2H$ atoms. These septets overlap in the spectrum of **3** but can be partially resolved by a change of solvent from $CDCl_3$ to C_6D_6.

Through a combination of ^1H, ^{13}C, and ^{29}Si NMR spectroscopy (see Tables 1 and 2) the structures of compounds **1**−**3** may be assigned unambiguously. The ^1H NMR spectra of **1**−**3** show a singlet and two doublets in the $Si-CH_3$ region of the spectra. This is consistent with the presence of one $OSiMe_2O$ and two $OSiMe_2H$ groups in each compound. Unfortunately, we are unable to differentiate between $OSiMe_2H_{(a)}$ and $OSiMe_2H_{(c)}$; see Scheme 1 for assignment. As is common with aluminum alkyls, it is difficult to observe the ^{13}C NMR spectra for the carbon directly bonded to the aluminum due to the quadrupolar broadening effect of the latter. The ^{13}C NMR spectra of compounds **1**−**3** show resonances for three $Si-CH_3$ species, two with $^1J(Si-C)$ coupling of ca. 60 Hz and one with ca. 72 Hz. In comparing the ^{13}C NMR spectrum of $[({}^tBu)_2Al(\mu\text{-}OSiMe_2H)]_2$ (see below), which has only an $OSiMe_2H$ group with a corresponding $^1J(Si-C)$ value of 59 Hz, we can differentiate between an $OSiMe_2H$ and an $OSiMe_2O$ group in compounds **1**−**3** (see Table 2).

In the $^{29}Si\{^1H\}$ NMR spectrum of compounds **1**−**3** three peaks are observed corresponding to three distinct silicon environments (e.g., Figure 1a). The ^1H-coupled ^{29}Si spectra of **1**−**3** allow for the assignment of each silicon environment and the connectivity of the siloxane backbone. For example, in **2** (Figure 1b) the two doublets of septets centered at 3.74 and −4.76 ppm are consistent with couplings to Si−H [$^1J(Si-H) = 206-209$ Hz] and $Si-CH_3$ [$^2J(Si-H) \approx 7$ Hz]. The resonance of $OSi_{(b)}(CH_3)_2O$ (−9.66 ppm) shows a rare $^3J(Si-H)$ coupling of 1.0 Hz (see Figure 1c). This allows us to conclude that one of the $OSiMe_2H$ groups is next to the $OSiMe_2O_{(b)}$ group, while one is isolated from the siloxane chain by the Al_2O_2 core. The deshielding of the Si nucleus in $OSi(CH_3)_2H$ caused by the proximity to the Al_2O_2 core

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[8] In both reactions other dichlorosiloxanes were observed as minor products.

[9] (a) Zhdanov, A. A.; Andriaov, K. A.; Bogdanova, A. A. *Izvest. Akad. Nauk, SSSR., Otdel., Khim. Nauk.* **1961**, 1261. (b) Ouchinnikov, Y. E.; Astapova, T. V.; Laurukhin, B. D.; Shklover, V. E.; Stuchkov, Y. T.; Zhdanov, A. A. *Zh. Struk. Khim.* **1986**, *27*, 120.

[10] We have recently isolated and structurally characterized the gallium analogue: McMahon, C. N.; Obrey, S. J.; Keys, A.; Bott, S. G.; Barron, A. R. Submitted for publication.

[11] Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1997**, *119*, 8387.

[12] $Mes^* = C_6H_2\text{-}2\text{-}4\text{-}6\text{-}{}^tBu_3$.

[13] For a reviews of metallocene catalysis, see: (a) Bochman, M., *J. Chem. Soc., Dalton Trans.* **1996**, 255. (b) Kaminsky, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1413.

[14] Sangokoya, S. A. US Patent 5,391,529, 1995.

[15] Smith, G, M.; Malpass, D. B.; Palmaka, S. W. US Patent 5,731,451, 1998.

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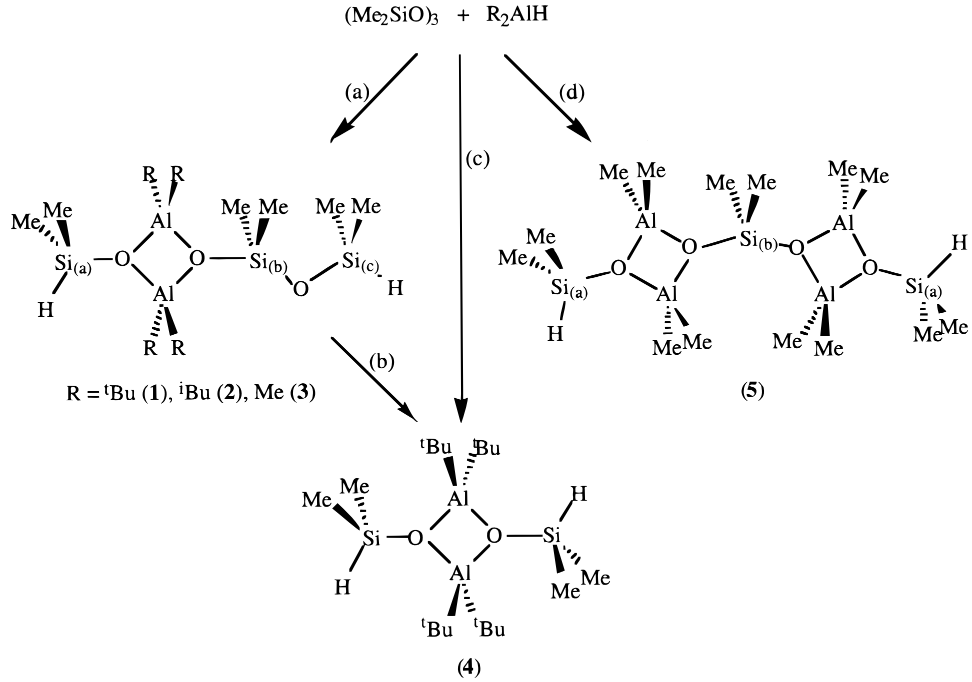
[17] Landry, C. C.; Davis, J. A.; Apblett, A. W.; Barron, A. R. *J. Mater. Chem.* **1993**, *3*, 567.

[18] It is widely known that reactions of AlR_3 result in leaching silicon grease, primeraly $(Me2SiO)_n$, from joints of stopcocks, see: Eisch, J. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1986; Vol. 1, p 668.

Scheme 1. Summary of Reactions of $(Me_2SiO)_3$ with R_2AlH[a]



[a] (a) Hexane, room temp, Si:Al = 1:2 for R = Me, (b) toluene, reflux w, $(^tBu)_2AlH$, (c) toluene, reflux, (d) hexane, room temp, Si:Al > 1.1.

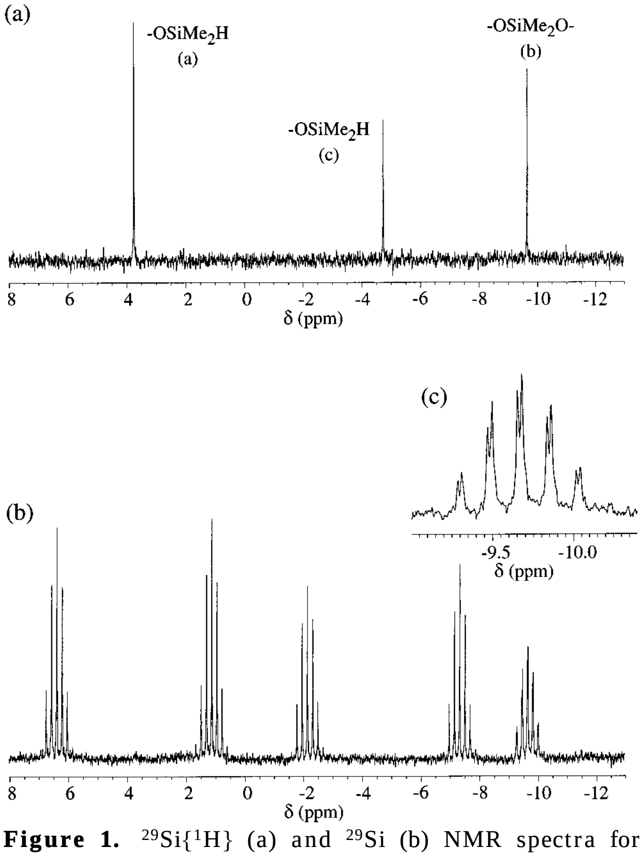


Figure 1. $^{29}Si\{^1H\}$ (a) and ^{29}Si (b) NMR spectra for $(^iBu)_2Al(\mu\text{-}OSiMe_2H)(\mu\text{-}OSiMe_2OSiMe_2H)Al(^iBu)_2$ (**2**) showing the presence of three distinct silicon environments. An expanded view of the resonance of $OSi(CH_3)_2O_{(b)}$ shows a rare ^3J(Si−H) coupling of 1.0 Hz (c, inset).

allows us to distinguish $Si_{(a)}$ (δ 3.74 ppm) from $Si_{(c)}$ (δ −4.76 ppm). We have previously observed this downfield shift for other aluminum siloxides (Al−O−Si) versus their siloxane (Si−O−Si) homologues.[4] The ^{27}Al NMR resonances for all compounds are all within four-coordinate range.

The molecular structure of compound **1** is shown in Figure 2; selected bond lengths and angles are given in Table 3. The structure consists of a planar Al_2O_2 core with asymmetric siloxide-bridging units and confirms the NMR assignment discussed above. The Al−O and Al−C distances in compound **1** (see Table 3) are within the ranges reported previously: 1.7−2.0 and 1.90−2.01 Å, respectively.[19] The Si−O distances to the siloxide oxygen are comparable to other siloxide compounds,[20] while those in the siloxane (see Table 3) are within the range reported for alkoxysilanes and disiloxanes.[21] It is interesting to note the difference in the orientation of the substituents on the siloxides. The O(2)−Si(2)−O(3)−Si(3) chain adopts a staggered *anti* conformation, with the methyl groups attached to Si(2) positioned symmetrically on either side of the chain; see Figure 2. Although the Al−O−Si angles about O(2) are close to equivalent (see Table 3), those around O(1) show a significant asymmetry, i.e., Al(1)−O(1)−Si(1) = 119.2(3)°, Al(2)−O(1)−Si(1) = 142.6(3)°, $\Delta = 23.4°$. A similar distortion has been observed previously in the structure of $[Me_2Al(\mu\text{-}OSiMe_2Ph)]_2$ ($\Delta = 4.3°$), but the magnitude observed in compound **1** is significantly larger. This

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[19] See for example: (a) Haaland, A. In *Coordination Chemistry of Aluminum*; Robinson G. H., Ed.; VCH: New York, 1993; Chapter 1. (b) Oliver, J. P.; Kumar, R. *Polyhedron* **1990**, *9*, 409.

[20] See for example: (a) Hursthouse, M. B.; Hossain, M. A. *Polyhedron* **1984**, *3*, 95. (b) Hursthouse, M. B.; Motevalli, M.; Sanganee, M.; Sullivan, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1709. (c) Motevalli, M.; Sanganee, M.; Savage, P. D.; Shah, S.; Sullivan, A. *J. Chem. Soc., Chem. Commun.* **1993**, 1132.

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Table 1. ^{1}H and ^{13}C NMR Data (298 K)^a

compound	^{1}H NMR^b				assignment^c	^{13}C NMR^d		assignment^c
1	4.89	sept	$^3J(H-H) = 3.0$	1H	$Si_{(a)}-H$ or $Si_{(c)}-H$	32.7		$C(CH_3)_3$
	4.73	sept	$^3J(H-H) = 3.0$	1H	$Si_{(a)}-H$ or $Si_{(c)}-H$	3.7	$^1J(Si-C) = 72$	$Si_{(b)}(CH_3)_2$
	0.99	s		36H	$C(CH_3)_3$	2.8	$^1J(Si-C) = 59$	$Si_{(a)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$
	0.48	d	$^3J(H-H) = 3.0$	6H	$Si_{(a)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$	0.9	$^1J(Si-C) = 60$	$Si_{(a)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$
	0.38	s		6H	$Si_{(b)}(CH_3)_2$			
	0.22	d	$^3J(H-H) = 3.0$	6H	$Si_{(a)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$			
2	4.78	sept	$^3J(H-H) = 3.0$	1H	$Si_{(a)}-H$ or $Si_{(c)}-H$	29.1		$CH_2CH(CH_3)_2$
	4.71	sept	$^3J(H-H) = 2.7$	1H	$Si_{(a)}-H$ or $Si_{(c)}-H$	26.3		$CH_2CH(CH_3)_2$
	1.81	m	$^3J(H-H) = 6.7$	4H	$CH_2CH(CH_3)_2$	2.0	$^1J(Si-C) = 72$	$Si_{(b)}(CH_3)_2$
	0.92	d	$^3J(H-H) = 6.6$	24H	$CH_2CH(CH_3)_2$	1.0	$^1J(Si-C) = 59$	$Si_{(a)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$
	0.34	d	$^3J(H-H) = 3.0$	6H	$Si_{(a)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$	0.9	$^1J(Si-C) = 60$	$Si_{(a)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$
	0.21	s		6H	$Si_{(b)}(CH_3)_2$			
	0.20	d	$^3J(H-H) = 2.7$	6H	$Si_{(c)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$			
	−0.03	d	$^3J(H-H) = 6.9$	8H	$CH_2CH(CH_3)_2$			
3	4.69	d, sept	$^3J(H-H) = 3.0$	2H	$Si_{(a)}-H$ and $Si_{(c)}-H$	1.2	$^1J(Si-C) = 72$	$Si_{(b)}(CH_3)_2$
	0.29	d	$^3J(H-H) = 3.0$	6H	$Si_{(a)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$	0.9	$^1J(Si-C) = 59$	$Si_{(a)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$
	0.19	d	$^3J(H-H) = 3.0$	6H	$Si_{(a)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$	0.35	$^1J(Si-C) = 59$	$Si_{(a)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$
	0.16	s		6H	$Si_{(b)}(CH_3)_2$			
	−0.79	s		12H	$C(CH_3)$			
4	4.86	sept	$^3J(H-H) = 3.0$	2H	$Si-H$	32.5		$C(CH)_3$
	1.01	s		36H	$C(CH_3)_3$	2.4	$^1J(Si-C) = 59$	$Si(CH_3)_2$
	0.47	d	$^3J(H-H) = 3.0$	12H	$Si(CH_3)_2$			
5	4.70	sept	$^3J(H-H) = 3.0$	2H	$Si_{(a)}-H$	1.61	$^1J(Si-C) = 72$	$Si_{(b)}(CH_3)_2$
	0.32	s		6H	$Si_{(b)}(CH_3)_2$	0.25	$^1J(Si-C) = 58$	$Si_{(a)}(CH_3)_2$
	0.29	d	$^3J(H-H) = 3.0$	12H	$Si_{(a)}(CH_3)_2$			
	−0.74	s		24H	(CH_3)			
6	4.89	d, sept	$^3J(H-H) = 3.0$	2H	$Si_{(a)}$-H or $Si_{(c)}$-H	32.7		$C(CH)_3$
	1.28	s		36H	$C(CH_3)_3$	4.1	$^1J(Si-C) = 72$	$Si_{(b)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$
	0.42	s		6H	$Si_{(b)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$	2.9	$^1J(Si-C) = 59$	$Si_{(a)}(CH_3)_2$ or $Si_{(d)}(CH_3)_2$
	0.32	d	$^3J(H-H) = 3.0$	6H	$Si_{(a)}(CH_3)_2$ or $Si_{(d)}(CH_3)_2$	1.3	$^1J(Si-C) = 74$	$Si_{(b)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$
	0.20	d	$^3J(H-H) = 3.0$	6H	$Si_{(a)}(CH_3)_2$ or $Si_{(d)}(CH_3)_2$	1.0	$^1J(Si-C) = 59$	$Si_{(a)}(CH_3)_2$ or $Si_{(d)}(CH_3)_2$
	0.13	s		6H	$Si_{(b)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$			
7	4.83	sept	$^3J(H-H) = 3.0$	2H	$Si_{(a)}-H$	29.3, 29.0		$CH_2CH(CH_3)_2$
	1.84	m	$^3J(H-H) = 7.0$	8H	$CH_2CH(CH_3)_2$	26.4		$CH_2CH(CH_3)_2$
	0.94	d	$^3J(H-H) = 6.5$	48H	$CH_2CH(CH_3)_2$	3.0	$^1J(Si-C) = 72$	$Si_{(b)}(CH_3)_2$
	0.40	s		6H	$Si_{(b)}(CH_3)_2$	1.2	$^1J(Si-C) = 58$	$Si_{(a)}(CH_3)_2$
	0.39	d	$^3J(H-H) = 3.0$	12H	$Si_{(a)}(CH_3)_2$			
	0.03	d	$^3J(H-H) = 7.0$	16H	$CH_2CH(CH_3)_2$			
8	4.91	sept	$^3J(H-H) = 3.0$	2H	$Si_{(a)}-H$	31.1^b		$C(CH_3)_3$
	1.01	s		72H	$C(CH_3)_3$	2.8^b	e	$Si_{(a)}(CH_3)_2$ or $Si_{(b)}(CH_3)_2$
	0.51	d	$^3J(H-H) = 3.0$	12H	$Si_{(a)}(CH_3)_2$	1.7^b	e	$Si_{(a)}(CH_3)_2$ or $Si_{(b)}(CH_3)_2$
	0.5	s		12H	$Si_{(b)}(CH_3)_2$			
9	4.81	d	$^3J(H-H) = 3.0$	2H	$Si_{(a)}-H$	29.2, 29.0		$CH_2CH(CH_3)_2$
	1.81	m	$^3J(H-H) = 6.6$	8H	$CH_2CH(CH_3)_2$	26.3		$CH_2CH(CH_3)_2$
	0.92	d	$^3J(H-H) = 6.6$	48H	$CH_2CH(CH_3)_2$	24.7		$CH_2CH(CH_3)_2$
	0.37	d	$^3J(H-H) = 3.0$	12H	$Si_{(a)}(CH_3)_2$	2.7	$^1J(Si-C) = 72$	$Si_{(b)}(CH_3)_2$
	0.30	s		12H	$Si_{(b)}(CH_3)_2$	1.1	$^1J(Si-C) = 58$	$Si_{(a)}(CH_3)_2$
	−0.2	d	$^3J(H-H) = 7.0$	16H	$CH_2CH(CH_3)_2$			
10	4.90	sept	$^3J(H-H) = 3.0$	1H	$Si_{(a)}-H$	72.4		OCH_2
	4.20	m		4H	OCH_2 (THF)	32.9		$C(CH_3)_3$
	2.08	m		4H	OCH_2CH_2 (THF)	31.5		$C(CH_3)_3$
	1.00	s		36H	$C(CH_3)_3$	25.0		OCH_2CH_2
	0.86	s		18H	$C(CH_3)_3$	4.7	$^1J(Si-C) = 71$	$Si_{(b)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$
	0.48	d	$^3J(H-H) = 3.0$	6H	$Si_{(a)}(CH_3)_2$	3.4	$^1J(Si-C) = 59$	$Si_{(a)}(CH_3)_2$
	0.41	s		6H	$Si_{(b)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$	3.0	$^1J(Si-C) = 74$	$Si_{(b)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$
	0.07	s		6H	$Si_{(b)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$			
11	1.07	s		36H	$C(CH_3)_3$	33.0		$C(CH_3)_3$
	0.48	s		18H	$Si(CH_3)_3$	5.3	$^1J(Si-C) = 59$	$Si(CH_3)_3$
12	4.89	sept	$^3J(H-H) = 3.0$	1H	$Si_{(a)}-H$ or $Si_{(c)}-H$	32.7		$C(CH_3)_3$
	0.48	d, d	$^3J(H-H) = 3.0$	12H	$Si_{(a)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$	5.3	$^1J(Si-C) = 60$	$Si_{(a)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$
	0.37	s		6H	$Si_{(a)}(CH_3)_2$ or $Si_{(b)}(CH_3)_2$	2.9	$^1J(Si-C) = 59$	$Si_{(a)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$
13	4.90	sept	$^3J(H-H) = 3.0$	1H	$Si_{(a)}-H$ or $Si_{(c)}-H$	32.7		$C(CH_3)_3$
	1.00	s		36H	$C(CH_3)_3$	4.4	$^1J(Si-C) = 59$	$Si_{(a)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$
	0.99	s		36H	$C(CH_3)_3$	4.2	$^1J(Si-C) = 73$	$Si_{(b)}(CH_3)_2$
	0.41	s		9H	$Si_{(b)}(CH_3)_2$	3.0	$^1J(Si-C) = 59$	$Si_{(a)}(CH_3)_2$ or $Si_{(c)}(CH_3)_2$
	0.13	s		9H	$Si_{(c)}(CH_3)_3$			

[a] 250 MHz; shift in ppm relative to $SiMe_4$ (external), coupling constants in Hz. [b] $CDCl_3$. [c] For key to assignments see Schemes 1−4. [d] C_6D_6. [e] Not detected.

distortion is clearly steric in nature, i.e., as a consequence of a ^{t}Bu···Me steric repulsion. A similar distortion is observed in $[(^tBu)_2Al(\mu\text{-}OSiMe_2H)]_2$; see below. The O(2)−Si(2)−O(3) and Si(2)−O(3)−Si(3) bond angles are within the ranges previously observed.[22−24]

Reaction of $(Me_2SiO)_3$ with $(^tBu)_2AlH$ in refluxing toluene yields the symmetric siloxide dimer $[(^tBu)_2Al(\mu\text{-}OSiMe_2H)]_2$ (**4**); see Scheme 1. As with compounds **1**−**3**, the IR spectrum of **4** has a single resonance for the ν_{Si-H} stretch (2157 cm^{-1}). The ^{1}H, ^{13}C, and ^{29}Si NMR

Table 2. ^{29}Si NMR Data (298 K)[a]

compound	^{29}Si NMR[b,c]				assignment[d]
1	5.17	d,sept	$^1J(Si-H) = 207$	$^2J(Si-H) = 7.1$	$Si_{(a)}-H$
	−3.86	d,sept	$^1J(Si-H) = 207$	$^2J(Si-H) = 7.1$	$Si_{(c)}-H$
	−8.1	sept,d	$^2J(Si-H) = 7.1$	$^3J(Si-H) = 1.5$	$Si_{(b)}Me_2$
2	3.74	d,sept	$^1J(Si-H) = 209$	$^2J(Si-H) = 7.2$	$Si_{(a)}-H$
	−4.76	d,sept	$^1J(Si-H) = 206$	$^2J(Si-H) = 7.1$	$Si_{(c)}-H$
	−9.66	sept,d	$^2J(Si-H) = 7.2$	$^3J(Si-H) = 1.0$	$Si_{(b)}Me_2$
3	4.08	d,sept	$^1J(Si-H) = 209$	$^2J(Si-H) = 7.2$	$Si_{(a)}-H$
	−4.73	d,sept	$^1J(Si-H) = 206$	$^2J(Si-H) = 7.1$	$Si_{(c)}-H$
	−9.97	sept,d	$^2J(Si-H) = 7.2$	$^3J(Si-H) = 0.9$	$Si_{(b)}Me_2$
4	5.5	d,sept	$^1J(Si-H) = 207$	$^2J(Si-H) = 7.1$	$Si-H$
5	4.66	d,sept	$^1J(Si-H) = 210$	$^2J(Si-H) = 7.1$	$Si_{(a)}-H$
	−3.65	sept	$^2J(Si-H) = 7.3$		$Si_{(b)}Me_2$
6	5.16	d,sept	$^1J(Si-H) = 207$	$^2J(Si-H) = 7.1$	$Si_{(a)}-H$
	−6.38	d,sept	$^1J(Si-H) = 205$	$^2J(Si-H) = 7.1$	$Si_{(d)}-H$
	−9.43	sept	$^2J(Si-H) = 7.2$		$Si_{(b)}Me_2$
	−17.19	sept,d	$^2J(Si-H) = 7.3$	$^3J(Si-H) = 0.9$	$Si_{(c)}Me_2$
7	4.77	d,sept	$^1J(Si-H) = 209$	$^2J(Si-H) = 7.1$	$Si_{(a)}-H$
	−4.74	sept	$^2J(Si-H) = 7.2$		$Si_{(b)}Me_2$
8	5.23	d,sept	$^1J(Si-H) = 208$	$^2J(Si-H) = 7.0$	$Si_{(a)}-H$
	−11.51	sept	$^2J(Si-H) = 7.1$		$Si_{(b)}Me_2$
9	4.25	d,sept	$^1J(Si-H) = 209$	$^2J(Si-H) = 7.2$	$Si_{(a)}-H$
	−12.06	sept	$^2J(Si-H) = 7.2$		$Si_{(b)}Me_2$
10	4.96	d,sept	$^1J(Si-H) = 207$	$^2J(Si-H) = 7.1$	$Si_{(a)}-H$
	−12.21	sept	$^2J(Si-H) = 7.2$		$Si_{(b)}Me_2$
	−24.26	sept	$^2J(Si-H) = 7.2$		$Si_{(c)}Me_2$
11	18.5	decet			$SiMe_3$
12	18.93	decet	$^2J(Si-H) = 6.6$		$Si_{(b)}Me_2$
	5.23	d,sept	$^1J(Si-H) = 207.2$	$^2J(Si-H) = 7.0$	$Si_{(a)}-H$
13	10.3	decet	$^2J(Si-H) = 6.7$		$Si_{(a)}Me_2$
	5.16	d,sept	$^1J(Si-H) = 207.1$	$^2J(Si-H) = 7.0$	$Si_{(c)}-H$
	−10.24	sept	$^2J(Si-H) = 7.1$		$Si_{(b)}Me_2$

[a] Chemical shift in ppm relative to $SiMe_4$ (external), coupling constants in Hz. [b] $CDCl_3$ solution. [c] Where multiple coupling occurs, the greater coupling constant is described first; for example, the description "d,sept" indicates the larger coupling is the doublet, the smaller a septet. [d] For key to assignments see Schemes 1−4.

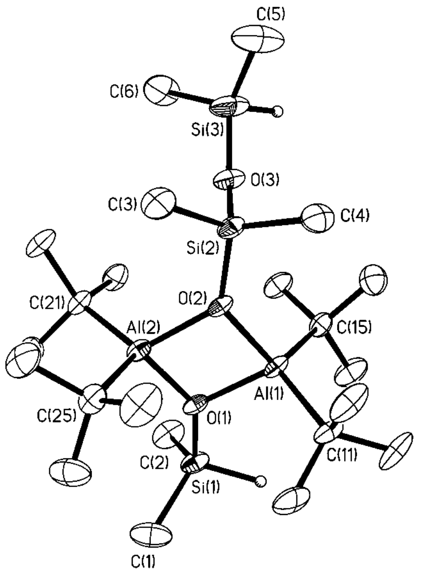

Figure 2. Molecular structure of $(^tBu)_2Al(\mu-OSiMe_2H)(\mu-OSiMe_2OSiMe_2H)Al(^tBu)_2$ (**1**). Thermal ellipsoids shown at the 20% level. Non-siloxide hydrogen atoms are omitted, and only one of the disordered positions of the methyl groups attached to Si(3) is shown, for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) in $(^tBu)_2Al(\mu-OSiMe_2H)-(\mu-OSiMe_2OSiMe_2H)Al(^tBu)_2$ (1)

Al(1)−O(1)	1.884(5)	Al(1)−O(2)	1.883(4)
Al(1)−C(11)	2.013(7)	Al(1)−C(15)	2.012(8)
Al(2)−O(1)	1.867(4)	Al(2)−O(2)	1.888(5)
Al(2)−C(21)	2.002(7)	Al(2)−C(25)	2.027(8)
Si(1)−O(1)	1.683(4)	Si(2)−O(2)	1.664(5)
Si(2)−O(3)	1.614(6)	Si(3)−O(3)	1.636(6)
O(1)−Al(1)−O(2)	81.9(2)	O(1)−Al(1)−C(11)	109.3(3)
O(1)−Al(1)−C(15)	115.2(3)	O(2)−Al(1)−C(11)	113.9(3)
O(2)−Al(1)−C(15)	112.6(3)	C(11)−Al(1)−C(15)	118.4(3)
O(1)−Al(2)−O(2)	82.3(2)	O(1)−Al(2)−C(21)	111.2(3)
O(1)−Al(2)−C(25)	113.7(3)	O(2)−Al(2)−C(21)	116.1(3)
O(2)−Al(2)−C(25)	112.5(3)	C(21)−Al(2)−C(25)	116.4(3)
Al(1)−O(1)−Al(2)	98.1(2)	Al(1)−O(1)−Si(1)	119.2(3)
Al(2)−O(1)−Si(1)	142.6(3)	Al(1)−O(2)−Al(2)	97.4(2)
Al(1)−O(2)−Si(2)	134.2(3)	Al(2)−O(2)−Si(2)	127.5(3)
O(2)−Si(2)−O(3)	106.3(3)	Si(2)−O(3)−Si(3)	149.9(4)

shifts observed for the single siloxide environment are consistent with the previous assignments on compounds **1**−**3** (see Tables 1 and 2). The molecular structure of $[(^tBu)_2Al(\mu-OSiMe_2H)]_2$ (**4**) was confirmed by X-ray crystallography, and its structure is shown in Figure 3; selected bond lengths and angles are given in Table 4. The quality of the data was insufficient to make any but a cursory commentary on its overall structure (see Experimental Section). The siloxide hydrogens are positioned in an *anti* conformation in a manner similar to the phenyl rings in $[Me_2Al(\mu-OSiMe_2Ph)]_2$.[4] It is interesting to note that the distortion observed about the dimethylsiloxide ($OSiMe_2H$) group in the structure of compound **1** is also seen in compound **4**, i.e., Δ(Al−O−Si) = 28° and 16°.

Compound **4** is also formed albeit in low yield from the reaction of $Al(^tBu)_3$ with $(Me_2SiO)_3$; see Experimental Section. The formation of a Si−*H* moiety is presum-

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(23) Hossain, M. A.; Hursthouse, M. B.; Ibrahim, A.; Mazid, M.; Sullivan, A. C. *J. Chem. Soc., Dalton Trans.* **1989**, 2347.

(24) Herrmann, W. A.; Stumpf, A. W.; Priermeier, T.; Bogdanovic, S.; Dufaud, V.; Basset, J.-M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2803.

Table 4. Selected Bond Lengths (Å) and Angles (deg) in $[(^tBu)_2Al(\mu\text{-}OSiMe_2H)_{1-x}(\mu\text{-}OSiMe_3)_x]_2$ ($x = 0, 0.5, 1$)

	$[(^tBu)_2Al(\mu\text{-}OSiMe_2H)]_2$ (**4**)	$[(^tBu)_2Al(\mu\text{-}OSiMe_3)]_2$ (**11**)	$(^tBu)_2Al(\mu\text{-}OSiMe_2H)(\mu\text{-}OSiMe_3)Al(^tBu)_2$ (**12**)
Al−O	1.87(1), 1.89(1)	1.884(3)	1.869(3), 1.880(4)
Si−O	1.76(2), 1.61(1)	1.685(3)	1.674(3)
O−Al−O	80.9(7), 80.2(6)	82.0(1)	82.1(2)
Al−O−Al	99.5(3)	97.9(1)	97.9(2)
Al−O−Si	116(1)−144(1)	130.2(2), 131.9(2)	130.2(2), 131.9(2)

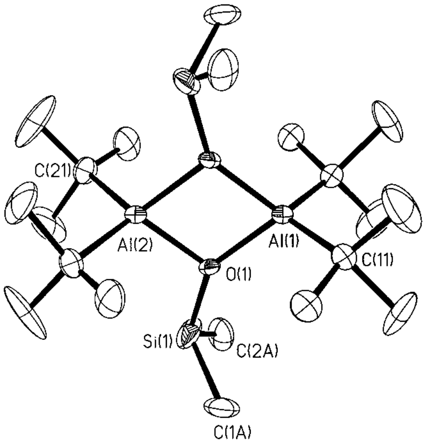


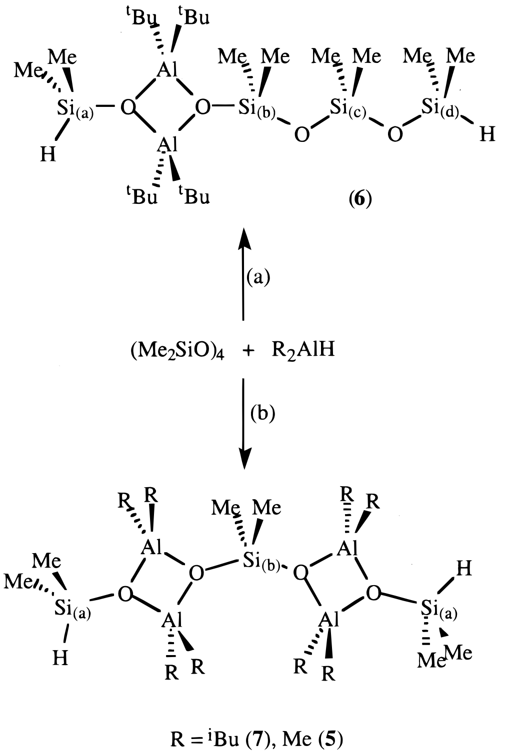
Figure 3. Molecular structure of $[(^tBu)_2Al(\mu\text{-}OSiMe_2H)]_2$ (**4**). Thermal ellipsoids are shown at the 20% level. Non-siloxide hydrogen atoms are omitted, and only one of the disordered positions of the methyl groups attached to Si(1) is shown, for clarity.

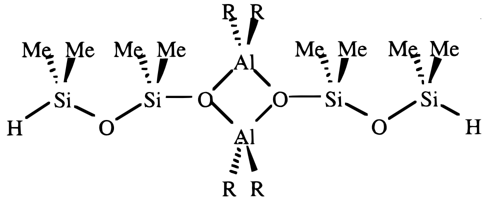
ably derived via b-hydrogen transfer from the aluminum *tert*-butyl group. Similar reactions have been previously reported for $AlEt_3$.[2] On the basis of the ^1H NMR of the reaction mixture, it appears that compound **4** is one of two aluminum siloxide containing products that are formed; however, we have been unable to characterize the second product.

As noted above, the reaction of Me_2AlH with $(Me_2SiO)_3$ forms compound **3** only when a Si:Al ratio of 0.5 is used in the reaction. If higher Si:Al ratios are employed, the product isolated is the tetra-aluminum siloxide-bridged compound, $[Me_2Al(\mu\text{-}OSiMe_2H)AlMe_2(\mu\text{-}OSiMe_2O)Me_2Al(\mu\text{-}OSiMe_2H)AlMe_2]$ (**5**); see Scheme 1. As **5** is a liquid, an X-ray structural characterization is not possible, but the presence of a $M^+ - Me$ peak in the MS, the IR spectrum, and a comparison of the NMR to related, structurally characterized compounds (see below) are sufficient to determine uniquely the molecular structure. The IR and ^1H NMR spectra of **5** exhibit single resonances (2147 cm^{-1} and 4.70 ppm, respectively) for the siloxane Si−*H*. The ^1H, ^{13}C, and ^{29}Si NMR shifts observed for the single $OSiMe_2H$ environment are consistent with our previous assignments for compounds **1**−**4** (see Tables 1 and 2). However, the ^{29}Si NMR peak for the central $OSiMe_2O$ group in **5** (−3.65 ppm) is significantly downfield of $OSiMe_2O$(b) compounds **1**−**3** (ca. −8 to −10 ppm) due to the added effect of a second Al_2O_2 group.

Reaction of R_2AlH with $(Me_2SiO)_4$. Reaction of $(^tBu)_2AlH$ with $(Me_2SiO)_4$ in hexane yields after 3 days at room temperature the asymmetrical siloxide compound $(^tBu)_2Al(\mu\text{-}OSiMe_2H)(\mu\text{-}OSiMe_2OSiMe_2OSiMe_2H)Al(^tBu)_2$ (**6**); see Scheme 2. The IR spectrum of compound **6** is similar to that of compound **1**, and a combination of ^1H, ^{13}C, and ^{29}Si NMR spectroscopy is necessary for the structure of compound **6** to be assigned unambiguously; see Tables 1 and 2. The presence of four distinct resonances in the ^{29}Si NMR spectrum of compound **6** implies the asymmetric species rather than the symmetrical siloxide (**III**). The deshielding effect of the Al_2O_2 core diminishes as its distance from the silicon nucleus increases, cf. $OSiMe_2O$(b) (−9.43 ppm), which is next to the Al_2O_2 core, versus $OSiMe_2O$(c) (−17.19 ppm), which has an intervening $OSiMe_2$ group. The ^3J(Si−H) coupling is again seen in the ^{29}Si NMR spectrum of **6**. The ^1H NMR spectral resolution did not allow us to observe this coupling in the ^{29}Si satellites of the $Si_{(d)}$−H septet.

Scheme 2. Summary of Reactions of $(Me_2SiO)_4$ with R_2AlH

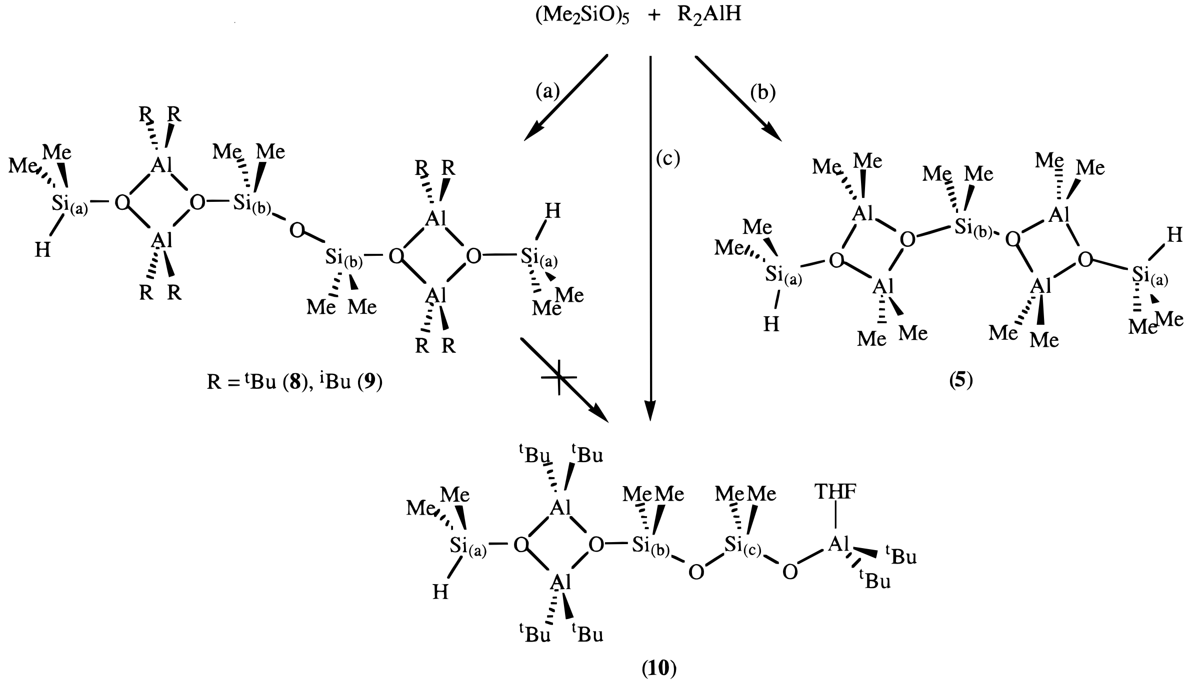




(**III**)

The reaction of Me_2AlH with $(Me_2SiO)_4$ yields the same product as formed with $(Me_2SiO)_3$ with high Si:Al ratios, i.e., compound **5**; see above. In contrast, $(^iBu)_2Al(\mu\text{-}OSiMe_2H)Al(^iBu)_2(\mu\text{-}OSiMe_2O)(^iBu)_2Al(\mu\text{-}OSiMe_2H)Al(^iBu)_2$ (**7**) is the only product isolated from the reaction of $(^iBu)_2AlH$ with $(Me_2SiO)_4$ (Scheme 2). As

Scheme 3. Summary of Reactions of $(Me_2SiO)_3$ with R_2AlH^a



^{a} (a) Hexane, room temp, (b) hexane, room temp, (c) hexane in the presence of THF.

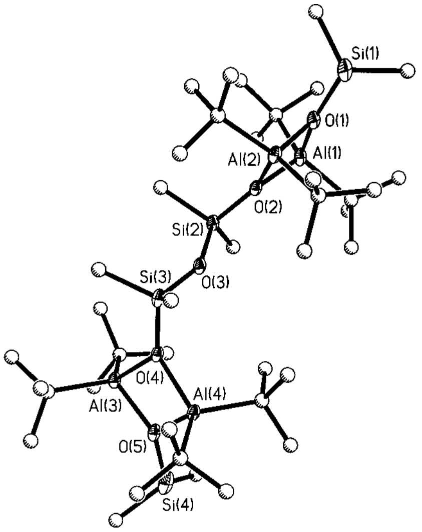
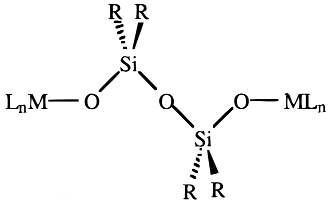


Figure 4. Molecular structure of $(^tBu)_2Al(\mu\text{-}OSiMe_2H)Al(^tBu)_2(\mu\text{-}OSiMe_2OSiMe_2O)(^tBu)_2Al(\mu\text{-}OSiMe_2H)Al(^tBu)_2$ (**8**). Thermal ellipsoids are shown at the 20% level. Non-siloxide hydrogen atoms are omitted for clarity.

expected, compound **7** is spectroscopically similar to compound **5**; see Tables 1 and 2. The methyl groups on each isobutyl ligand are diastereotopic, caused by prochiral inequivalence. Thus two signals are observed for $CH_2CH(CH_3)_2$ in the ^{13}C NMR spectrum. However, to see the corresponding doublet of doublets in the ^1H NMR spectrum for two inequivalent $CH_2CH(CH_3)_2$, the spectrum must be collected in C_6D_6 [1.21, 1.20 ppm, $J(H-H) = 6.5, 6.5$ Hz]. It is assumed that accidental overlap accounts for the single doublet observed for **7** in $CDCl_3$ (as reported in Table 1).

Reaction of R_2AlH with $(Me_2SiO)_5$. The reaction of R_2AlH (R = ^tBu, ^iBu) with $(Me_2SiO)_5$ yields the siloxide-bridged compounds $[R_2Al(\mu\text{-}OSiMe_2H)AlR_2(\mu\text{-}OSiMe_2OSiMe_2O)R_2Al(\mu\text{-}OSiMe_2H)AlR_2]$, R = ^tBu, (**8**) and ^iBu (**9**). The reaction with Me_2AlH again yields compound **5**; see Scheme 3.

The molecular structure of **8**, as determined by X-ray crystallography, is shown in Figure 4; selected bond lengths and angles are given in Table 5. The structure consists of two Al_2O_2 cycles connected by a symmetric disiloxide unit. Similar bridging $-OSiR_2OSiR_2O-$ units have been previously observed in both transition metal and main group chemistry (**IV**).[25] It is interesting to note the orientation of the two Al_2O_2 cycles with respect to the O−Si−O−Si−O bridge; the structure is that of Al_2O_2 steps. The O(2)−Si(2)−O(3)−Si(3)−O(4) chain adopts a staggered *anti* conformation. The O(2)−Si(2)−O(3) bond angle in **8** is significantly larger than those in compound **1**, although the Si(2)−O(3)−Si(3) angle is unchanged as compared to compound **1**.



ML_n = $SnMe_3$, $Mo(N)(CH_2{}^tBu)_3$, ReO_3
(**IV**)

On the basis of a comparison of the NMR spectra, compounds **8** and **9** are clearly isostructural. The IR spectra of compounds **8** and **9** each show a band consistent with a ν_{Si-H} stretch [2146 cm^{-1} (**8**), 2151 cm^{-1} (**9**)]. The ^1H NMR spectra each show a single septet due to two equivalent silicon hydrides. On the basis of the ^1H, ^{13}C, and ^{29}Si NMR spectroscopy the structures of compounds **8** and **9** observed in the solid state (see

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[25] Gosink, H.-J.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Irmer, E.; Herbst-Irmer, R. *Organometallics* **1994**, *13*, 3420.

Table 5. Selected Bond Lengths (Å) and Angles (deg) in $(^tBu)_2Al(\mu\text{-}OSiMe_2H)Al(^tBu)_2(\mu\text{-}OSiMe_2H)Al(^tBu)_2$ (8)

Al(1)−O(1)	1.869(4)	Al(1)−O(2)	1.922(3)
Al(1)−C(11)	2.026(6)	Al(1)−C(15)	2.014(6)
Al(2)−O(1)	1.873(3)	Al(2)−O(2)	1.896(4)
Al(2)−C(21)	2.026(6)	Al(2)−C(25)	1.991(5)
Al(3)−O(4)	1.895(4)	Al(3)−O(5)	1.870(4)
Al(3)−C(31)	2.017(4)	Al(3)−C(35)	2.007(5)
Al(4)−O(4)	1.918(4)	Al(4)−O(5)	1.872(4)
Al(4)−C(41)	1.993(4)	Al(4)−C(45)	2.040(5)
Si(1)−O(1)	1.672(4)	Si(2)−O(2)	1.668(3)
Si(2)−O(3)	1.638(3)	Si(3)−O(3)	1.633(3)
Si(3)−O(4)	1.674(4)	Si(4)−O(5)	1.676(4)

O(1)−Al(1)−O(2)	82.7(1)	O(1)−Al(1)−C(11)	114.9(2)
O(1)−Al(1)−C(15)	108.0(2)	O(2)−Al(1)−C(11)	112.0(2)
O(2)−Al(1)−C(15)	118.4(2)	C(11)−Al(1)−C(15)	116.2(2)
O(1)−Al(2)−O(2)	83.3(1)	O(1)−Al(2)−C(21)	110.0(2)
O(1)−Al(2)−C(25)	114.6(2)	O(2)−Al(2)−C(21)	114.7(2)
O(2)−Al(2)−C(25)	110.7(2)	C(21)−Al(2)−C(25)	118.5(2)
O(4)−Al(3)−O(5)	83.2(2)	O(4)−Al(3)−C(31)	113.0(2)
O(4)−Al(3)−C(35)	116.3(2)	O(5)−Al(3)−C(31)	114.1(2)
O(5)−Al(3)−C(35)	108.3(2)	C(31)−Al(3)−C(35)	117.1(2)
O(4)−Al(4)−O(5)	82.5(2)	O(4)−Al(4)−C(41)	109.8(2)
O(4)−Al(4)−C(45)	118.6(2)	O(5)−Al(4)−C(41)	116.0(2)
O(5)−Al(4)−C(45)	108.0(2)	C(41)−Al(4)−C(45)	117.2(2)
Al(1)−O(1)−Al(2)	98.0(2)	Al(1)−O(1)−Si(1)	143.6(2)
Al(2)−O(1)−Si(1)	118.5(2)	Al(1)−O(2)−Al(2)	95.4(1)
Al(1)−O(2)−Si(2)	124.2(2)	Al(2)−O(2)−Si(2)	139.6(1)
Al(3)−O(4)−Al(2)	95.6(2)	Al(3)−O(4)−Si(3)	129.0(2)
Al(4)−O(4)−Si(3)	135.3(2)	Al(3)−O(5)−Al(4)	98.0(2)
Al(3)−O(5)−Si(4)	142.6(2)	Al(4)−O(5)−Si(4)	119.3(2)
Si(2)−O(3)−Si(3)	149.3(2)	O(2)−Si(2)−O(3)	110.8(2)
O(3)−Si(4)−O(4)	111.3(2)		

above) are retained in solution. In particular, the ^{29}Si (proton-coupled) NMR spectrum shows a septet due to the bridging $OSiMe_2O$ groups and a doublet of septets for the $OSiMe_2H$ end groups. The absence of a ^3J(Si−H) coupling precludes the presence of an $OSiMe_2OSiMe_2H$ group. It is interesting to note that there is no evidence for hindered rotation about the central $O-SiMe_2-O-SiMe_2-O$ bridge, as all methyl groups are equivalent in the ^1H and ^{13}C NMR spectra.

If the reaction of $(^tBu)_2AlH$ with $(Me_2SiO)_5$ is carried out in the presence of THF, $(^tBu)_2Al(\mu\text{-}OSiMe_2H)Al(^tBu)_2(\mu\text{-}OSiMe_2OSiMe_2O)Al(^tBu)_2(THF)$ (**10**) may be isolated (Scheme 3). However, addition of THF to compound **8** does not form compound **10**, indicating that compound **10** is not a simple Lewis base cleavage product.

The molecular structure of compound **10** is shown in Figure 5; selected bond lengths and angles are given in Table 6. The structure consists of an Al_2O_2 cycle bridged to a mono-aluminum center through a disiloxide unit. The planar aluminum dimer is also bridged by a $OSiMe_2H$ moiety. All distances are within their expected ranges. It is interesting to note the differences between compounds **8** and **10** as evidenced by the orientation of the Al_2O_2 cycles with respect to the O−Si−O−Si−O bridge. The O(2)−Si(2)−O(3)−Si(3)−O(4) chain in compound **10** adopts a *gauche* conformation as compared to the *anti* conformation observed in compound **8**.

Reaction of $(^tBu)_2AlH$ with Linear Siloxanes. To gain further understanding of the reaction of dialkylaluminum hydrides with cyclic siloxanes, we have investigated the reaction of $(^tBu)_2AlH$ with the linear siloxanes $(Me_3Si)_2O$ and $Me_3Si(OSiMe_2)_2OSiMe_3$.

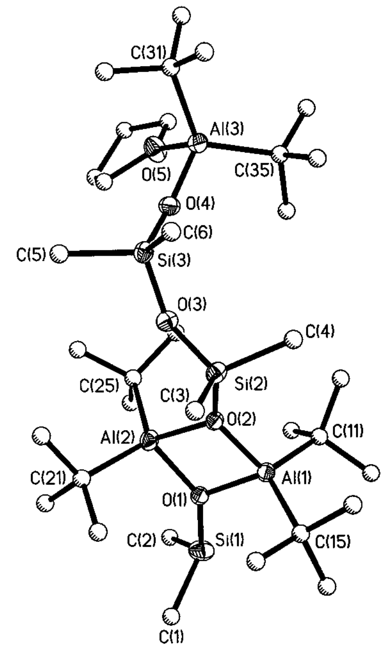

Figure 5. Molecular structure of $(^tBu)_2Al(\mu\text{-}OSiMe_2H)Al(^tBu)_2(\mu\text{-}OSiMe_2OSiMe_2O)Al(^tBu)_2(THF)$ (**10**). Thermal ellipsoids are shown at the 20% level. Non-siloxide hydrogen atoms are omitted for clarity.

Table 6. Selected Bond Lengths (Å) and Angles (deg) in $(^tBu)_2Al(\mu\text{-}OSiMe_2H)Al(^tBu)_2(\mu\text{-}OSiMe_2OSiMe_2O)Al(^tBu)_2(THF)$ (10)

Al(1)−O(1)	1.874(8)	Al(1)−O(2)	1.885(8)
Al(1)−C(11)	2.02(1)	Al(1)−C(15)	1.00(1)
Al(2)−O(1)	1.885(8)	Al(2)−O(2)	1.895(8)
Al(2)−C(21)	1.98(2)	Al(2)−C(25)	2.03(1)
Al(3)−O(4)	1.724(9)	Al(3)−O(5)	1.94(1)
Al(3)−O(31)	1.98(2)	Al(3)−C(35)	1.97(1)
Si(1)−O(1)	1.684(8)	Si(2)−O(2)	1.674(8)
Si(2)−O(3)	1.622(8)	Si(3)−O(3)	1.647(8)
Si(3)−O(4)	1.589(9)		

O(1)−Al(1)−O(2)	82.8(3)	O(1)−Al(1)−C(11)	110.6(5)
O(1)−Al(1)−C(15)	113.9(5)	O(2)−Al(1)−C(11)	116.3(5)
O(2)−Al(1)−C(15)	111.7(5)	C(11)−Al(1)−C(15)	116.9(5)
O(1)−Al(2)−O(2)	82.3(3)	O(1)−Al(2)−C(21)	110.0(5)
O(1)−Al(2)−C(25)	113.7(5)	O(2)−Al(2)−C(21)	115.9(5)
O(2)−Al(2)−C(25)	111.1(5)	C(21)−Al(2)−C(25)	118.4(6)
O(4)−Al(3)−O(5)	96.9(4)	O(4)−Al(3)−C(31)	113.7(6)
O(4)−Al(3)−C(35)	110.6(5)	O(5)−Al(3)−C(31)	105.3(6)
O(5)−Al(3)−C(35)	107.0(5)	C(31)−Al(3)−C(35)	120.4(6)
Al(1)−O(1)−Al(2)	97.5(4)	Al(1)−O(1)−Si(1)	120.6(5)
Al(2)−O(1)−Si(1)	141.9(5)	Al(1)−O(2)−Al(2)	96.8(4)
Al(1)−O(2)−Si(2)	136.6(5)	Al(2)−O(2)−Si(2)	126.4(4)
Si(2)−O(3)−Si(3)	142.1(5)	Al(3)−O(4)−Si(3)	160.4(5)
O(2)−Si(2)−O(3)	106.2(4)	O(3)−Si(4)−O(4)	110.7(4)

Reaction of $(^tBu)_2AlH$ with an excess of $(Me_3Si)_2O$ resulted in the formation of the symmetric siloxide product $[(^tBu)_2Al(\mu\text{-}OSiMe_3)]_2$ (**11**). The NMR spectroscopic characterization of compound **11** is given in Tables 1 and 2. It is worth noting the similarity of the ^{29}Si NMR spectrum of compound **11** (18.5 ppm) to that of its methyl analogue, $[Me_2Al(\mu\text{-}OSiMe_3)]_2$ (19.0 ppm), that has been previously prepared.[4,5,26] The molecular structure of $[(^tBu)_2Al(\mu\text{-}OSiMe_3)]_2$ (**11**), as determined by X-ray crystallography, is shown in Figure 6; selected bond lengths are given in Table 4.

The reaction of the noncyclic siloxane $Me_3Si(OSiMe_2)_2OSiMe_3$ with $(^tBu)_2AlH$ yields a mixture of $(^tBu)_2Al(\mu\text{-}OSiMe_2H)(\mu\text{-}OSiMe_3)Al(^tBu)_2$ (**12**) and $(^tBu)_2Al(\mu\text{-}OSiMe_2H)(\mu\text{-}OSiMe_2OSiMe_3)Al(^tBu)_2$ (**13**); see Scheme 4 and the Experimental Section. Compounds **12** and **13** could

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(26) Schmidbaur, H. *J. Organomet. Chem.* **1963**, *1*, 28.

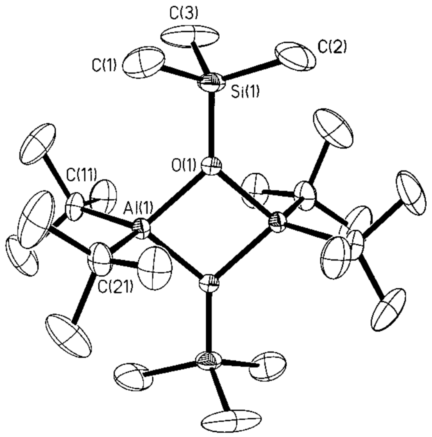
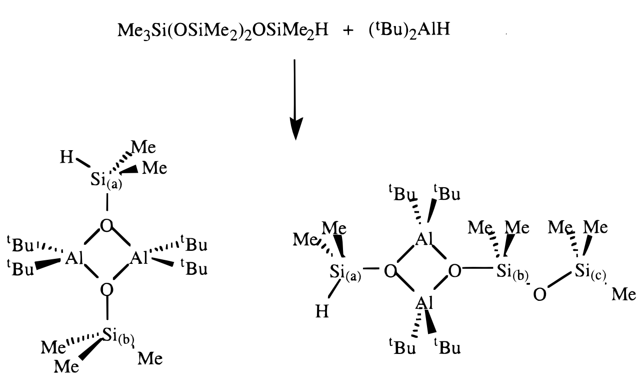


Figure 6. Molecular structures of $[(^tBu)_2Al(\mu\text{-}OSiMe_3)]_2$ (**11**). Thermal ellipsoids are shown at the 30% level. Hydrogen atoms are omitted for clarity.

Scheme 4. Reaction of $Me_3Si(OSiMe_2)_2OSiMe_3$ with $(^tBu)_2AlH$



(**12**) (**13**)

not be fully separated by fractional crystallization (see below). However, the ^1H, ^{13}C, and ^{29}Si NMR spectra allow full spectral assignment. For example, the $^{29}Si\{^1H\}$ NMR spectrum of the reaction mixture shows five distinct silicon peaks. The proton-coupled ^{29}Si NMR spectrum allows these to be assigned to two $OSiMe_3$ groups, two $OSiMe_2H$ groups, and a single $OSiMe_2O$ environment. The absence of a $^3J(Si-H)$ coupling precludes the $OSiMe_2O$ being adjacent to a $OSiMe_2H$ group; therefore an $OSiMe_2OSiMe_3$ must be present in one product. By comparison of the chemical shifts to compounds discussed above and similar siloxane species, such as $HMe_2SiOSiMe_2OSiMe_3$ and $Me_3Si(OSiMe_2)_2OSiMe_3$, we can again use the deshielding effect of Al_2O_2 to determine that only one $OSiMe_3$ is next to an Al_2O_2 core and thus distinguish $OSi_{(b)}Me_3$ (compound **12**) from $OSi_{(c)}Me_3$ (compound **13**). Only separation of these species would allow unambiguous assignments $OSi_{(a)}Me_2H$ (compound **12**) and $OSi_{(c)}Me_2H$ (compound **13**); see Scheme 4 for assignments.

Although compound **13** could not be isolated in a pure form, a few crystals of $(^tBu)_2Al(\mu\text{-}OSiMe_2H)(\mu\text{-}OSiMe_3)Al(^tBu)_2$ (**12**) were isolated, and the structure was determined by X-ray crystallography. The molecular structure is shown in Figure 7; selected bond lengths and angles are given in Table 4.

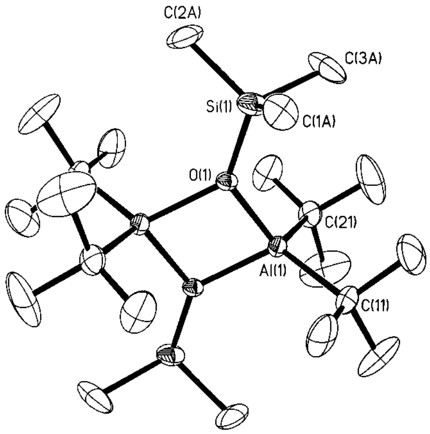


Figure 7. Molecular structures of $(^tBu)_2Al(\mu\text{-}OSiMe_3)(\mu\text{-}OSiMe_2H)Al(^tBu)_2$ (**12**). Thermal ellipsoids are shown at the 30% level. Hydrogen atoms are omitted for clarity.

How Do Aluminum Hydrides React with Dimethylsiloxanes? Part of the rationale for this study was furthering the understanding of the reaction pathway involved in the cleavage of siloxanes by aluminum reagents, especially hydrides. On the basis of the observation of multiple siloxane side products, we have previously proposed that the reaction of $AlMe_3$ with $(Me_2SiO)_3$ and $(Me_2SiO)_n$ occurs via the direct removal of a "Me_2SiO" from the siloxane chain.[4] On the basis of the work described herein, such a random clipping of the siloxane chain is clearly not an acceptable mechanism. However, the proposal[2,4] that the first step of the reaction involves the coordination of the siloxane to the aluminum to form a Lewis acid–base complex is clearly significant.

We have recently demonstrated[27] that coordination of alcohols to aluminum results in the activation of the O*H* group dramatically increasing its Brönsted acidity, as measured by a decrease in pK_a of about 7! A similar β-substituent activation was also observed for the complexation of organic carbonyls to aluminum.[28] In each of these cases a simple measure of the activation was provided by the appropriate NMR spectrum of the ligand in comparing free and coordinated forms. For example, complexation of water ($\delta = 3.36$ ppm in Et_2O) to an aluminum trialkyl results in a significant downfield shift to 7.75–8.15 ppm (depending on the identity of the alkyl substituent[29]). With regard to siloxanes we have previously reported that the ^{29}Si NMR resonance for $(Me_2SiO)_3$ (−9.6 ppm) is shifted downfield upon coordination to aluminum in $Me_3Al(Me_2SiO)_3$ (−5.4 ppm[30]). Thus, it is reasonable to propose that coordination of a siloxane to aluminum results in the increased electrophilicity of the adjacent silicon atoms (**V**) and hence increase its receptivity to hydride attack.

To develop a rational description of the hydride transfer reactions in cyclic siloxanes and polysiloxanes, it is best to first consider the simplest disiloxane, (Me3-

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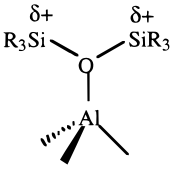
[27] McMahon, C. N.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1997**, 3129.

[28] (a) Power, M. B.; Nash, J. R.; Healy, M. D.; Barron, A. R. *Organometallics* **1992**, *11*, 1830. (b) Power, M. B.; Bott, S. G.; Clark, D. L.; Atwood, J. L.; Barron, A. R. *Organometallics* **1990**, *9*, 3086. (c) Power, M. B.; Bott, S. G.; Atwood, J. L.; Barron, A. R. *J. Am. Chem. Soc.* **1990**, *112*, 3446.

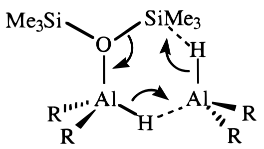
[29] Boleslawski, M.; Serwatowski, J. *J. Organomet. Chem.* **1983**, *255*, 269.

[30] It should be noted that since $Me_3Al(Me_2SiO)_3$ is fluxional at room temperature, the observed NMR shift is a time average value of one uncomplexed and two complexed Si environments. Thus, the actual NMR shift of the "activated" silicon is actually closer to −3 ppm.

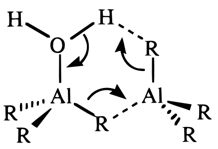


(**V**)

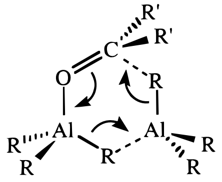
Si)$_2$O. Thus, as is shown in Scheme 5, the reaction of $(Me_3Si)_2O$ with R_2AlH will occur via the initial formation of the activated Lewis acid–base complex; subsequent hydride transfer results in the formation of “$R_2Al(OSiMe_3)$” and Me_3SiH. Given our previous studies,[27,31] it is far more likely that instead of a four-membered transition state (see Scheme 5), the reaction will involve hydride attack from a second uncomplexed molecule of R_2AlH, via a six-membered transition state (**VI**) similar to that proposed for the hydrolysis of AlR_3 (**VII**)[27] and the alkylation of ketones (**VIII**).[28] However, for the sake of clarity all subsequent schemes will adopt the intramolecular hydride transfer with the caveat that in the absence of detailed kinetic data the molecularity of the hydride transfer transition state is as yet uncertain.



(**VI**)

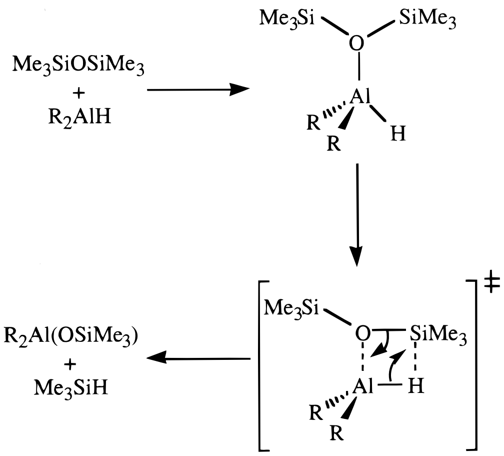


(**VII**)



(**VIII**)

Scheme 5. Proposed Reaction Pathway for the Reaction of $(Me_3Si)_2O$ with R_2AlH



If we apply the pathway shown in Scheme 5 to the reaction between $(Me_2SiO)_3$ and R_2AlH, then complexation and hydride transfer will result in ring opening and the formation of “$R_2Al(OSiMe_2OSiMe_2OSiMe_2H)$”; see Scheme 6. Although coordination of additional R_2AlH may, in theory, occur at any of the siloxane oxygens, steric hindrance suggests that the γ oxygen is most likely, i.e., that furthest from the R_2Al moiety. Coordination to the γ oxygen may result in hydride transfer to either the β or γ silicon. While the former is more likely on steric grounds and provides an adequate explanation of all subsequent products, we cannot rule out hydride transfer to the γ silicon. In fact such a process clearly occurs during the reaction of R_2AlH with $(Me_2SiO)_5$; see below. Hydride transfer to the β silicon results in the formation of two aluminum-containing products “$R_2Al(OSiMe_2H)$” and “$R_2Al(OSiMe_2OSiMe_2H)$”; see Scheme 6. These are clearly the two fragments required to construct compounds **1**–**3**. As is shown in Scheme 6, subsequent coordination of R_2AlH to the siloxane oxygen of “$R_2Al(OSiMe_2OSiMe_2H)$” may result in hydrogen transfer to either silicon. Hydride transfer to the siloxide silicon results in the formation of compound **4**, while hydride transfer to the siloxane silicon provides the “$R_2Al(OSiMe_2O)AlR_2$” fragment required for the formation of compound **5**. The absence of any evidence for the formation of the *tert*-butyl and isobutyl analogues of compound **5** may be explained on steric grounds. Thus, sterically hindered aluminum alkyl substituents favor the transition state for the formation of **1**–**3** since it minimizes any Al–R···R–Al interactions.

A similar reaction scheme may be proposed for the isolation of compound **6** from the reaction of $(^t\mathrm{Bu})_2AlH$ with $(Me_2SiO)_4$. Initial formation of “$(^t\mathrm{Bu})_2Al(OSiMe_2OSiMe_2OSiMe_2OSiMe_2H)$” results from ring opening, while subsequent cleavage forms “$(^t\mathrm{Bu})_2Al(OSiMe_2OSiMe_2OSiMe_2H)$” and “$(^t\mathrm{Bu})_2Al(OSiMe_2H)$”, which are the constituent fragments of compound **6**. We presume that with the reactions of $(Me_2SiO)_4$ with $(^i\mathrm{Bu})_2AlH$ or Me_2AlH further cleavage of the “$R_2Al(OSiMe_2OSiMe_2OSiMe_2H)$” fragment is possible due to the lower steric interactions.

The absence of silanes other than Me_2SiH_2 and the exclusive formation of compounds **8** and **9** from the reactions of $(Me_2SiO)_5$ with $(^t\mathrm{Bu})_2AlH$ and $(^i\mathrm{Bu})_2AlH$, respectively, suggests that once the siloxane ring has been opened, subsequent scission occurs exclusively from the $OSiMe_2H$ termini. Initial ring opening of $(Me_2SiO)_5$ will yield the “$R_2Al(OSiMe_2)_4OSiMe_2H$” fragment. If the subsequent chain scission occurred with the formation the “$R_2Al(OSiMe_2OSiMe_2O)AlR_2$” fragment, necessary for compounds **8** and **9**, then the silane side product, $HSiMe_2OSiMe_2OSiMe_2H$, would be formed. We have not observed any such species. Thus, it would appear that the “$R_2Al(OSiMe_2)_4OSiMe_2H$” fragment is consecutively cleaved to form “$R_2Al(OSiMe_2)_3OSiMe_2H$” and “$R_2Al(OSiMe_2)_2OSiMe_2H$” along with the concurrent formation of the “$R_2AlOSiMe_2H$” fragment.

We may conclude that, in general, the reaction of R_2AlH with cyclic siloxanes $(Me_2SiO)_n$ occurs via (a) ring cleavage, followed by (b) stepwise chain scission. Where long aluminum siloxide–siloxane chains are formed, e.g., “$(^t\mathrm{Bu})_2Al(OSiMe_2)_nOSiMe_2H$”, $n \geq 3$, chain scission occurs one silicon at a time, starting from the terminal

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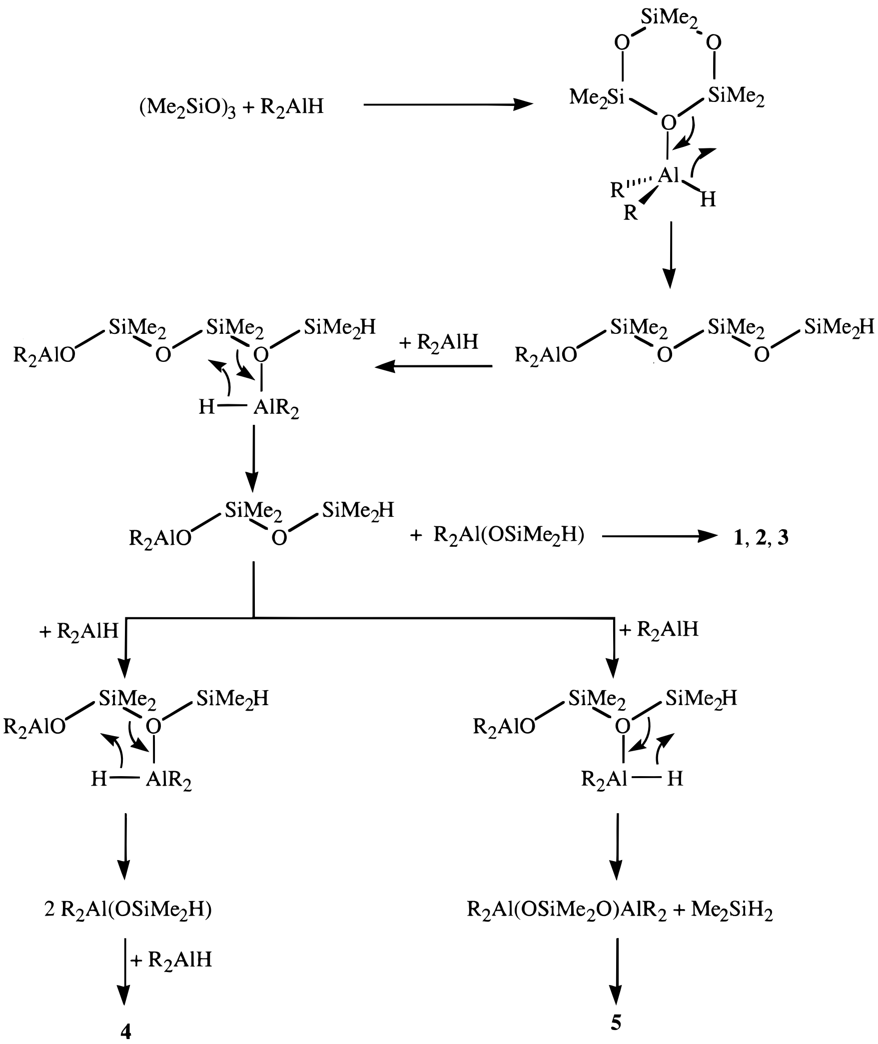
(31) We have calculated that in the case of the hydrolysis of aluminum alkyls the activation energy required for the formation of a four-membered transition state (98 kJ mol^{-1}) is higher than ligand dissociation (84–95 kJ mol^{-1}), Barron, A. R. Unpublished results.

Scheme 6. Proposed Pathway for the Formation of Compounds 1–5 from the Reaction of $(Me_2SiO)_3$ with R_2AlH



silicon unit. In the case of low molecular weight noncyclic polysiloxanes [e.g., $Me_3Si(OSiMe_2)_nOSiMe_3$] initial chain cleavage most likely occurs at the chain termini, resulting in the formation of the aluminum siloxide fragment, "$R_2Al(OSiMe_2H)$", and a new hydride-terminated polysiloxane, $Me_3Si(OSiMe_2)_{n-1}OSiMe_2H$. However, with high molecular weight noncyclic polysiloxanes [e.g., $Me_3Si(OSiMe_2)_nOSiMe_3$, $n \rightarrow \infty$] initial chain cleavage is more likely to occur randomly along the polymer backbone. If this occurs, then an aluminum siloxide fragment, "$R_2Al(OSiMe_2)_mOSiMe_2H$" ($m \geq 0$), and a new hydride-terminated polysiloxane, $Me_3Si(OSiMe_2)_{n-m}OSiMe_2H$, will be formed. Subsequent chain scission will eventually yield siloxide compounds of the types described herein.

It is interesting to postulate that the cleavage of polysiloxanes with aluminum alkyls and hydrides is of a general reaction type and may be applied to related systems. In particular, it is possible that the reaction of $Ga(^tBu)_3$ with elemental sulfur (S_8), to form $[(^tBu)_2Ga(\mu\text{-}SS^tBu)]_2$,[32] occurs in an analogous manner to that of R_2AlH with $(Me_2SiO)_4$. We are continuing our investigations in this area.

Experimental Section

Mass spectra were obtained on a Finnigan MAT 95 mass spectrometer operating with an electron beam energy of 70 eV for EI mass spectra. IR spectra (4000–400 cm^{-1}) were obtained using a Nicolet 760 FT-IR infrared spectrometer. IR samples were prepared as Nujol mulls between KBr plates unless otherwise stated. NMR spectra were obtained on Bruker AM-250 and Avance 200 spectrometers using (unless otherwise stated) benzene-d_6 solutions. Chemical shifts are reported relative to internal solvent resonances (^1H and ^{13}C) and external $[Al(H_2O)_6]^{3+}$ (^{27}Al) and $SiMe_4$ (^{29}Si). The relaxation times for different Si environments in the $^{29}Si\{^1H\}$ spectrum are variable, precluding accurate integration. An optimum relaxation delay was determined to be 30 s.

Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY. Molecular weight measurements were made in CH_2Cl_2 with the use of an instrument similar to that described by Clark.[33] The syntheses of $(^tBu)_2AlH$ and $Al(^tBu)_3$ were performed according to modification of the literature methods.[34] Me_2AlH and $(^iBu)_2AlH$ were generously donated by Akzo Nobel. All siloxanes were obtained from United Chemical Technologies or Aldrich and [except for $(Me_2SiO)_4$ and $(Me_2SiO)_5$, which were dried prior to use] were used without further purification.

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[32] Power, M. B.; Ziller, J. W.; Tyler, A. N.; Barron, A. R. *Organometallics* **1992**, *11*, 1055.

[33] Clark, E. P. *Ind. Eng. Chem. Anal. Ed.* **1941**, *13*, 820.

[34] (a) Uhl, W. *Z. Anorg. Allg. Chem.* **1989**, *570*, 37. (b) Lehmkuhl, H.; Olbrysch, O.; Nehl, H. *Liebigs Ann. Chem.* **1973**, 708. (c) Lehmkuhl, H.; Olbrysch, O. *Liebigs Ann. Chem.* **1973**, 715.

$(^t\text{Bu})_2\text{Al}(\mu\text{-OSiMe}_2\text{H})(\mu\text{-OSiMe}_2\text{OSiMe}_2\text{H})\text{Al}(^t\text{Bu})_2$ (1). A solution of $(^t\text{Bu})_2\text{AlH}$ (0.8 g, 5.7 mmol) in hexane (50 mL) and was added to $(\text{Me}_2\text{SiO})_3$ (0.62 g, 2.8 mmol). The reaction was stirred for 4 days, filtered, and brought to dryness in vacuo. The product was recrystallized from hexane, and X-ray quality crystals were grown from a pentane solution (less than 10 mL) at −78 °C. Yield: 76%. Mp: 75 °C (subl). Anal. (calc, %): C 52.4 (52.1), H 11.2 (11.1). MS (EI, %): *m/z* 449 ($\text{M}^+ - {}^t\text{Bu}$, 100), 393 ($\text{M}^+ - 2\,{}^t\text{Bu}$, 32). IR ($\text{cm}^{-1}$): 2149 (s, Si−H), 1261 (s), 1052 (s, br), 906 (s), 821 (s, br).^{27}Al (CDCl_3): δ 128 ($W_{1/2}$ = 4066 Hz).

$(^i\text{Bu})_2\text{Al}(\mu\text{-OSiMe}_2\text{H})(\mu\text{-OSiMe}_2\text{OSiMe}_2\text{H})\text{Al}(^i\text{Bu})_2$ (2). A solution (2.75 wt %) of $(^i\text{Bu})_2\text{AlH}$ (8.8 g, 9.0 mmol) in heptane was added to $(\text{Me}_2\text{SiO})_3$ (1.0 g, 4.5 mmol), and the reaction was stirred for 3 days. The desired product was isolated as a colorless solid by removal of heptane in vacuo. Yield: 92%. Anal. (calc, %): C 51.9 (52.1) H: 11.3 (11.1). MS (EI, %): *m/z* 449 ($\text{M}^+ - {}^i\text{Bu}$, 70), 393 ($\text{M}^+ - 2\,{}^i\text{Bu}$, 62), 337 ($\text{M}^+ - 3\,{}^i\text{Bu}$, 27), 59 ($\text{OSiMe}_2\text{H}$, 70). IR (neat, cm^{-1}): 2955 (s), 2859 (s), 2150 (Si−H, s), 1462 (br s), 1399 (s), 1360 (s), 1319 (s), 1260 (s), 1180 (s). ^{27}Al (CDCl_3): δ 168 ($W_{1/2}$ = 7390 Hz).

$(\text{Me})_2\text{Al}(\mu\text{-OSiMe}_2\text{H})(\mu\text{-OSiMe}_2\text{OSiMe}_2\text{H})\text{Al}(\text{Me})_2$ (3). Neat Me_2AlH (0.4 g, 6.9 mmol) was added to $(\text{Me}_2\text{SiO})_3$ (1.09 g, 4.9 mmol) in hexane (30 mL). The solution was stirred for 4 days. Removal of the solvent followed by vacuum distillation yielded a colorless liquid. Yield: 81%. Anal. (calc, %): C 36.1 (35.5), H 10.0 (9.5). MS (EI, %): *m/z* 323 ($\text{M}^+ - \text{Me}$, 16), 249 ($\text{M}^+ - 2\,\text{Me} - \text{SiMe}_2\text{H}$, 24), 189 ($\text{M}^+ - 2\,\text{Me} - 2\,\text{SiMe}_2\text{H}$, 100), 175 ($\text{Me}_2\text{Al}_2\text{O}_2\text{SiMe}_2$, 55). IR (neat, cm^{-1}): 2963 (s), 2933 (s), 2892 (s), 2145 (s, Si−H), 1419 (m), 1262 (s), 1195 (s), 1078 (s). ^{27}Al (CDCl_3): δ 150 ($W_{1/2}$ = 2880 Hz).

$[(^t\text{Bu})_2\text{Al}(\mu\text{-OSiMe}_2\text{H})]_2$ (4). Method 1. To a toluene (200 mL) solution of $(\text{Me}_2\text{SiO})_3$ (1.5 g, 6.8 mmol) was added $\text{Al}(^t\text{Bu})_3$ (4.0 g, 20.2 mmol). The reaction was refluxed for 4 days. The toluene was removed in vacuo and repeated recrystallization with hexane at −23 °C yielded white crystals. Yield: 0.8 g, 18%.

Method 2. A mixture of $(^t\text{Bu})_2\text{AlH}$ (0.3 g, 2.1 mmol) and $(\text{Me}_2\text{SiO})_3$ (0.23 g, 1.0 mmol) was refluxed in toluene (100 mL) overnight. After removal of the volatiles under vacuum, the residue was recrystallized from hexane (10 mL) at −23 °C. Yield: 68%. Mp: >230 °C. Anal. (calc, %): C 36.0 (36.3), H 9.9 (9.5). MS (EI, %): *m/z* 375 ($\text{M}^+ - {}^t\text{Bu}$, 20), 59 ($^t\text{Bu} + 2$, 100). IR ($\text{cm}^{-1}$): 2157 (s, Si−H), 1260 (s), 1066 (m, br), 840 (s), 810 (s).

$\text{Me}_2\text{Al}(\mu\text{-OSiMe}_2\text{H})\text{AlMe}_2(\mu\text{-OSiMe}_2\text{O})\text{Me}_2\text{Al}(\mu\text{-OSiMe}_2\text{H})\text{-AlMe}_2$ (5). Method 1. Neat Me_2AlH (0.30 g, 5.1 mmol) was added to a hexane (30 mL) solution of $(\text{Me}_2\text{SiO})_3$ (0.54 g, 2.4 mmol). The solution was stirred for 4 days. The solvent was removed under vacuum. Yield: 22%.

Method 2. Neat Me_2AlH (0.30 g, 5.1 mmol) was added to a hexane (30 mL) solution of $(\text{Me}_2\text{SiO})_4$ (0.38 g, 1.3 mmol). The solution was stirred for 4 days. The solvent was removed, and two new products were present by ^1H NMR. The minor (undetermined) product was removed by distillation under vacuum, leaving the pure product. Yield: 90%.

Method 3. Neat Me_2AlH (0.55 g, 9.6 mmol) was added to $(\text{Me}_2\text{SiO})_5$ (0.7 g, 1.9 mmol) in hexane (30 mL). After stirring for 4 days the volatiles were removed under vacuum to yield a colorless liquid. Yield: 68%. Anal. (calc, %): C 36.0 (35.9), H 9.5 (9.5). MS (EI, %): *m/z* 453 ($\text{M}^+ - \text{Me}$, 2), 395 ($\text{M}^+ - \text{Me} - \text{SiMe}_2$, 5), 381 ($\text{M}^+ - 2\,\text{Me} - \text{SiMe}_2$, 100), 321 ($\text{M}^+ - 2\,\text{Me} - 2\,\text{SiMe}_2\text{H}$, 10), 175 ($\text{Me}_2\text{Al}_2\text{O}_2\text{SiMe}_2$, 18). IR (neat, cm^{-1}): 2931 (s), 2893 (m), 2147 (Si−H, s), 1418 (m), 1261 (s), 1200 (s), 910 (s). ^{27}Al (CDCl_3): δ 157 ($W_{1/2}$ = 3381 Hz).

$(^t\text{Bu})_2\text{Al}(\mu\text{-OSiMe}_2\text{H})(\mu\text{-OSiMe}_2\text{OSiMe}_2\text{OSiMe}_2\text{H})\text{Al}\text{-}(^t\text{Bu})_2$ (6). A hexane (50 mL) solution of $(^t\text{Bu})_2\text{AlH}$ (0.5 g, 3.6 mmol) was added to $(\text{Me}_2\text{SiO})_4$ (0.52 g, 1.8 mmol). After stirring at room temperature for 4 days, the solution was filtered and brought to dryness in vacuo. The product was purified by recrystallized from hexane at −78 °C. Yield: 38%. Anal. (calc, %): C 50.0 (49.6), H 11.1 (10.8). MS (EI, %): *m/z* 523 ($\text{M}^+ - {}^t\text{Bu}$, 100), 509 ($\text{M}^+ - {}^t\text{Bu} - \text{Me}$, 10), 467 ($\text{M}^+ - 2\,{}^t\text{Bu}$, 10), 307 ($\text{M}^+ - 3\,{}^t\text{Bu} - \text{AlOSiMe}_2\text{H}$, 28). IR ($\text{cm}^{-1}$): 2145 (s, Si−H), 1474 (s), 1385 (m), 1263 (s), 1059 (br s).

$(^i\text{Bu})_2\text{Al}(\mu\text{-OSiMe}_2\text{H})\text{Al}(^i\text{Bu})_2(\mu\text{-OSiMe}_2\text{O})(^i\text{Bu})_2\text{Al}(\mu\text{-O-SiMe}_2\text{H})\text{Al}(^i\text{Bu})_2$ (7). A 2.75% solution of $(^i\text{Bu})_2\text{AlH}$ (6.65 g, 2.3 mmol) in heptane was added to $(\text{Me}_2\text{SiO})_4$ (1.0 g, 3.4 mmol), and the reaction was stirred for 4 days. The desired product was isolated by removal of heptane in vacuo and was a pure colorless oil. Yield: 50%. Anal. (calc, %): C 57.0 (56.7), H 11.3 (11.5). MS (EI, %): *m/z* 747 ($\text{M}^+ - {}^i\text{Bu}$, 40), 531 ($\text{M}^+ - 4\,{}^i\text{Bu} - 3\,\text{Me}$, 63). IR (neat, cm^{-1}): 2949 (s), 2868 (s), 2152 (s, br, Si−H), 1463 (s), 1400 (m), 1377 (m), 1363 (m), 1320 (m), 1262 (s), 1183 (s), 1079 (s, br).

$(^t\text{Bu})_2\text{Al}(\mu\text{-OSiMe}_2\text{H})\text{Al}(^t\text{Bu})_2(\mu\text{-OSiMe}_2\text{OSiMe}_2\text{O})(^t\text{Bu})_2\text{-Al}(\mu\text{-OSiMe}_2\text{H})\text{Al}(^t\text{Bu})_2$ (8). $(^t\text{Bu})_2\text{AlH}$ (0.4 g, 0.94 mmol) was dissolved in hexane (50 mL) and added to $(\text{Me}_2\text{SiO})_5$ (0.52 g, 1.4 mmol). The reaction was stirred for 4 days, filtered, and brought to dryness in vacuo. The crude residue showed unreacted $(\text{Me}_2\text{SiO})_5$ and the desired product, which was purified by recrystallization from pentane at −78 °C. Yield: 44%. Mp: 185−187 °C. Anal. (calc, %): C 54.2 (54.6), H 11.2 (11.2). IR (cm^{-1}): 2160, 2146 (m, Si−H), 1259 (s), 1025 (s, br), 909 (s). ^{27}Al (CDCl_3): δ 148 ($W_{1/2}$ = 2200 Hz).

$(^i\text{Bu})_2\text{Al}(\mu\text{-OSiMe}_2\text{H})\text{Al}(^i\text{Bu})_2(\mu\text{-OSiMe}_2\text{OSiMe}_2\text{O})(^i\text{Bu})_2\text{Al-}(\mu\text{-OSiMe}_2\text{H})\text{Al}(^i\text{Bu})_2$ (9). A 2.75% solution of $(^i\text{Bu})_2\text{AlH}$ (5.78 g, 6.0 mmol) in heptane was added to $(\text{Me}_2\text{SiO})_5$ (1.0 g, 2.7 mmol), and the reaction was stirred for 3 days. Removal of the volatiles yielded a colorless oil. Yield: 84%. Anal. (calc, %): C 54.7 (54.6), H 11.4 (11.2). MS (EI, %): *m/z* 821 ($\text{M}^+ - {}^i\text{Bu}$, 42), 765 ($\text{M}^+ - 2\,{}^i\text{Bu}$, 20), 605 ($\text{M}^+ - 4\,{}^i\text{Bu} - \text{SiMe}_2\text{H}$, 100). IR (neat) ($\text{cm}^{-1}$): 2946 (s), 2866 (s), 2151 (s, SiH), 1462 (s), 1401 (m), 1362 (m), 1319 (m), 1264 (s), 1086 (s, br), 905 (s).

$(^t\text{Bu})_2\text{Al}(\mu\text{-OSiMe}_2\text{H})\text{Al}(^t\text{Bu})_2(\mu\text{-OSiMe}_2\text{OSiMe}_2\text{O})\text{Al}(^t\text{Bu})_2\text{-(THF)}$ (10). $(\text{Me}_2\text{SiO})_5$ (0.52 g, 1.4 mmol) and $(^t\text{Bu})_2\text{AlH}$ (0.4 g, 2.79 mmol) were added together neat, and hexane (ca. 20 mL) contaminated with THF was added. The reaction was stirred for 3 days. The solution was filtered and placed in the freezer, yielding a white solid. Upon recrystallization from hexane at −23 °C needlelike crystals formed. Yield: 66%. Mp: 124−127 °C. Anal. (calc, %): C 54.8 (55.4), H 11.0 (11.1). IR (cm^{-1}): 2141 (s, Si−H), 1262 (s), 1076 (s), 1025 (s), 914 (s), 834 (s, br).

$[(^t\text{Bu})_2\text{Al}(\text{OSiMe}_3)]_2$ (11). To $(^t\text{Bu})_2\text{AlH}$ (0.1 g, 0.69 mmol) was added a large excess of $(\text{Me}_3\text{Si})_2\text{O}$ (ca. 10 mL). The solution was initially clear; however, after stirring for 4 days a white precipitate had formed. The precipitate was filtered and dried in vacuo. Yield: 82%. Mp: >200 °C. Anal. (calc, %): C 35.4 (35.9), H 12.0 (11.8). MS (EI, %): *m/z* 403 ($\text{M}^+ - {}^t\text{Bu}$, 100), 347 ($\text{M}^+ - 2\,{}^t\text{Bu}$, 10). IR ($\text{cm}^{-1}$): 1257 (s), 843 (s), 810 (m), 769 (s). ^{27}Al (CDCl_3): δ 124 ($W_{1/2}$ = 2490 Hz).

$(^t\text{Bu})_2\text{Al}(\mu\text{-OSiMe}_2\text{H})(\mu\text{-OSiMe}_3)\text{Al}(^t\text{Bu})_2$ (12) and $(^t\text{Bu})_2\text{-Al}(\mu\text{-OSiMe}_2\text{H})(\mu\text{-OSiMe}_2\text{OSiMe}_3)\text{Al}(^t\text{Bu})_2$ (13). $\text{Me}_3\text{Si}(\text{OSiMe}_2)_2\text{OSiMe}_3$ (0.344 g, 1.1 mmol) was added neat to $(^t\text{Bu})_2\text{AlH}$ (0.3 g, 0.7 mmol) in hexane (30 mL). The reaction was stirred for 3 days and brought to dryness in vacuo. The white sticky solid was recrystallized from hexane (ca. 5 mL) at −23 °C.

Crystallographic Studies. Crystals of compounds **1**, **4**, **8**, **10**, **11**, and **12** were sealed in a glass capillary under argon and mounted on the goniometer of an Enraf-Nonius CAD-4 (**8**), a Rigaku AFC-5S (**1**, **4**, and **10**), or a Bruker CCD SMART system (**11** and **12**), equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and corrected for Lorentz and polarization effects. Data collection and cell determinations were performed in a manner previously described.[35] The locations of the majority of non-hydrogen atoms were obtained by using either SIR (for **1**)[36] or SHELXS-86,[37] while the

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Table 7. Summary of X-ray Diffraction Data

	$(^{t}Bu)_2Al(\mu\text{-}OSiMe_2H)(\mu\text{-}OSiMe_2OSiMe_2H)Al(^{t}Bu)_2$ (**1**)	$[(^{t}Bu)_2Al(\mu\text{-}OSiMe_2H)]_2$ (**4**)
empir formula	$C_{22}H_{56}Al_2O_3Si_3$	$C_{20}H_{50}Al_2O_2Si_2$
cryst size, mm	0.24 × 0.21 × 0.17	0.05 × 0.06 × 0.12
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$C2$
a, Å	10.026(2)	16.527(3)
b, Å	11.468(2)	11.100(2)
c, Å	15.347(3)	8.835(2)
α, deg	96.67(3)	
β, deg	90.56(3)	120.52(3)
γ, deg	110.59(3)	
V, Å^3	1638.5(6)	1396.3(5)
Z	2	2
D(calcd), g/cm^3	1.028	1.033
μ, cm^{-1}	2.20	2.00
temp, K	298	298
2θ range, deg	4.5−45.0	4.6−55.0
no. collected	4484	2972
no. ind	4291	2733
no. obsd	2561 ($\lvert F_o\rvert > 4.0\sigma\lvert F_o\rvert$)	1217 ($\lvert F_o\rvert > 4.0\sigma\lvert F_o\rvert$)
weighting scheme	SHELXTL 0.1065, 6.501	SHELXTL 0.532, 1.741
R	0.084	0.195
R_w	0.264	0.452
largest diff peak, e Å^{-3}	0.55	1.82

	$(^{t}Bu)_2Al(\mu\text{-}OSiMe_2H)Al(^{t}Bu)_2\text{-}(\mu\text{-}OSiMe_2H)Al(^{t}Bu)_2$ (**8**)	$(^{t}Bu)_2Al(\mu\text{-}OSiMe_2H)Al(^{t}Bu)_2\text{-}(\mu\text{-}OSiMe_2OSiMe_2O)Al(^{t}Bu)_2(THF)$ (**10**)
empir formula	$C_{48}H_{98}Al_4O_5Si_4$	$C_{34}H_{81}Al_3O_5Si_3$
cryst size, mm	0.15 × 0.18 × 0.25	0.11 × 0.21 × 0.22
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	11.4925(9)	14.720(3)
b, Å	15.125(1)	16.563(3)
c, Å	17.958(2)	10.333(2)
α, deg	111.234(8)	91.51(3)
β, deg	101.612(7)	110.09(3)
γ, deg	98.867(7)	85.44(3)
V, Å^3	2760.5(3)	2358.5(8)
Z	2	2
D(calcd), g/cm^3	1.058	1.04
μ, cm^{-1}	2.00	1.90
temp, K	298	298
2θ range, deg	3.0−45.0	4.0−45.0
no. collected	7204	4678
no. ind	7204	4440
no. obsd	3991 ($\lvert F_o\rvert > 6.0\sigma\lvert F_o\rvert$)	2221 ($\lvert F_o\rvert > 4.0\sigma\lvert F_o\rvert$)
weighting scheme	$w^{-1} = 0.04(\lvert F_o\rvert)^2 + \sigma(\lvert F_o\rvert)^2$	SHELXTL 0.086, 16.023
R	0.0431	0.093
R_w	0.0465	0.217
largest diff peak, e Å^{-3}	0.43	0.50

	$[(^{t}Bu)_2Al(\mu\text{-}OSiMe_3)]_2$ (**11**)	$(^{t}Bu)_2Al(\mu\text{-}OSiMe_2H)(\mu\text{-}OSiMe_3)Al(^{t}Bu)_2$ (**12**)
empir formula	$C_{22}H_{54}Al_2O_2Si_2$	$C_{21}H_{52}Al_2O_2Si_2$
cryst size, mm	0.14 × 0.11 × 0.13	0.10 × 0.23 × 0.12
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a, Å	9.594(2)	9.571(2)
b, Å	15.767(3)	15.903(3)
c, Å	10.461(2)	10.375(2)
α, deg		
β, deg	109.82(5)	109.34(3)
γ, deg		
V, Å^3	1488.7(5)	1489.5(2)
Z	2	2
D(calcd), g/cm^3	1.028	1.00
μ, cm^{-1}	1.92	1.90
temp, K	298	298
2θ range, deg	5.0−46.6	4.5−46.6
no. collected	6680	6735
no. ind	2148	2156
no. obsd	1677 ($\lvert F_o\rvert > 4.0\sigma\lvert F_o\rvert$)	822 ($\lvert F_o\rvert > 4.0\sigma\lvert F_o\rvert$)
weighting scheme	SHELXTL 0.208, 0.503	SHELXTL 0.21, 0.0
R	0.0911	0.077
R_w	0.2591	0.199
largest diff peak, e Å^{-3}	0.81	0.34

remaining atomic coordinates were determined through the generation of difference Fourier maps using MolEN[38] or SHELXTL-93.[39] Disorder was noted in several instances. One of the terminal $SiMe_2H$ groups in compound **1** appeared on difference maps with three peaks bonded to the silicon in a tetrahedral arrangement, in which one peak was twice as large as the other two. These latter peaks refined well as half-occupancy carbons, implying an interchange between one methyl and the hydride. It was possible to resolve only one of the two hydride positions, however. The $SiMe_2H$ groups in compound **4** were disordered over two sites in a 1:1 ratio as a result of the deviation of the silicon atoms from the O(1)$\cdots$O(1′) vector due to the steric interactions between the $SiMe_2H$ group and the aluminum *tert*-butyl substituents. It is interesting to note that there is no symmetry relationship between the two disordered sites. Although compounds **11** and **12**, which differ only by replacement of a silicon methyl by a hydride, are isomrphous, the behavior of the $SiMe_2X$ groups is different. In compound **11**, the three carbon atoms (the molecule resides over a center of inversion) were located, while in compound **12**, six equal positions were observed. These were refined as being 5/6 C and 1/6 H. All non-hydrogen atoms were treated with anisotropic thermal parameters, except in compound **10**, for which sufficient data were available to treat only the Al, Si, O atoms and the C atoms of the THF ligand in this fashion. The hydrogen atoms attached to the silicons in compound **8** were located and refined with isotropic thermal parameters. All other hydrogen atoms were included with fixed thermal parameters and constrained to "ride" upon the appropriate atoms [d(C−H) = 0.95 Å]. A summary of cell parameters, data collection, and structure solution is given in Table 7. Scattering factors were taken from ref 40. The data for compound **4** were of very low precision due to a very weakly scattering crystal that also showed significant anisotropic decay. Accordingly, only the crystal data are reported for this compound.

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Supporting Information Available: Full listings of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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